225
227
233

15

QUARTERLY OF APPLIED MATHEMATICS

Vol. XXXIV OCTOBER 1976 No. 3

VARIATIONAL-LAGRANGIAN IRREVERSIBLE THERMODYNAMICS OF NONLINEAR THERMORHEOLOGY*

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Abstract. A principle of virtual dissipation generalizing d'Alembert's principle to nonlinear irreversible thermodynamics provides a unifying foundation which leads to an extremely general variational-Lagrangian analysis of dissipative phenomena. Thus a synthesis is achieved between thermodynamics and classical mechanics. The present paper applies this principle to the nonlinear thermomechanics of continua with dissipation and heat conduction. Field equations, constitutive equations and Lagrangian equations with generalized coordinates are derived for nonlinear thermoviscoelastcity, nonlinear thermoelasticity and heat conduction, plasticity, and compressible heat conducting fluids with Newtonian and non-Newtonian viscosity. The thermodynamics of instability is also analyzed from the same fundamental viewpoint.

1. Introduction. A Lagrangian-variational approach to irreversible thermodynamics was initiated by the author in 1954–55 [1, 2]. It was developed mainly in the context of linearity and applied to thermoelasticity [3, 4] viscoelasticity [1, 2, 4], porous media [5], and initially stressed porous and continuous media [6, 7]. The applicability of these methods to nonlinear problems was demonstrated in a variety of special cases, such as heat transfer [8], porous solids [9] and nonlinear thermoelasticity [10]. A treatment of nonlinear viscoelasticity based on a Lagrangian thermodynamic approach has also been presented by Schapery [11].

The theory embodied in the publications cited above provides a unified analysis based on Lagrangian formalism and generalized coordinates. Among many advantages, the equations have the same form in any coordinate system. Thus basic reciprocity properties of linear dissipative systems are immediately evident for a very large class of phenomena and boundary conditions. As a consequence, the proof of reciprocity properties does not have to be established for each particular case. Basic properties for systems with heredity are also obtained from the concept of internal coordinates and a general expression derived for the associated operator formalism. The corresponding

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* Received February 7, 1975. This research was sponsored by the Air Force Office of Scientific Research (N.A.M.) through the European Office of Aerospace Research and Development (AFSC), United States Air Force, under contract F 44620-71-C-0092.

electric circuit analogy is the impedance of a "black box" containing resistor capacitor elements. In addition, this unified analysis is based on a fundamental thermodynamic approach.

These methods also provide a fundamental invariance in the expression of physical laws much more general than the traditional tensor invariance, since it includes the field variables as a particular case of generalized coordinates.

The variational principle has recently been extended and referred to as a *principle of virtual dissipation* [12]. It encompasses the whole field of nonlinear thermodynamics of irreversible systems and constitutes a generalization of d'Alembert's principle of classical mechanics. It should be pointed out that its application provides the field equations governing the physical system. This is in contrast with formal variational procedures which are based on a knowledge of the field equations. As in classical mechanics, the principle may be expressed in Hamiltonian form and leads to Lagrangian equations. A brief description of these results is provided in Secs. 2 and 3. This includes a discussion of the "collective potential" already introduced earlier [1, 2] in the analysis of systems at non-uniform temperature. Two forms of dissipation must also be considered: *relative* and *intrinsic dissipation.* The entropy is separated into two terms, the supplied and produced entropy, the first being associated with the concept of entropy displacement as defined earlier [3].

Note that the use of a displacement vector for both entropy and material points plays an important role in unifying the theory. As pointed out in a more detailed paper [12], quasi-reversible systems, while nonlinear and far from equilibrium, may be considered as nearly reversible, so that Onsager's principle becomes applicable. This may be embodied in a *principle of virtual thermodynamic equilibrium* where reverse dissipative forces are applied in analogy with the reverse inertia forces of d'Alembert's principle.

The purpose of the present paper is to apply the thermodynamic principle of virtual dissipation to the thermomechanics of nonlinear dissipative media including heat conduction.

Nonlinear thermoviscoelastic media are considered in Secs. 4 and 5 as a particular case of quasi-reversible systems. Temperatures and stresses are expressed in terms of large deformations and entropy supplied and produced. Heating due to dissipation is included. Field equations and Lagrangian equations are also obtained directly. Results derived earlier [1, 2, 4] in linear viscoelasticity are shown to be a particular case and are briefly recalled in Sec. 6.

In Sec. 7 the principle is applied to derive isothermal stress-strain relations for viscoelastic-plastic materials and the closely related case of materials with internal failures.

In Sec. 8 a completely general nonlinear thermoelastic theory with finite deformations and temperature changes is derived. It yields new field equations and Lagrangian equations. This generalizes the results obtained for the quasi-isothermal case [10]. The variational Lagrangian formulation of nonlinear heat conduction originated in 1957 and included in a later book [8] is shown to be a consequence of thermodynamics through the principle of virtual dissipation. In the linear case this result is self-evident [3].

Sec. 9 considers compressible viscous fluids with heat conduction for both Newtonian and non-Newtonian viscosity. Application of the virtual dissipation principle leads to field and Lagrangian equations. A simplified derivation of non-Newtonian constitutive equations is given in the Appendix. The particular case of small isothermal displacements of an incompressible Newtonian fluid leads to "linear viscodynamics", discussed in Sec. 10. This is the analogue of linear viscoelasticity except that now viscosity and inertia are the two physical features instead of viscosity and elasticity. The use of internal coordinates introduces the concept of "viscodynamic operator" in analogy with viscoelastic operators and already obtained and used earlier in the context of porous media [5, 6].

The thermodynamics of unstable systems is analyzed in Sec. 11. Two cases are distinguished. In the first the system is initially in a state of unstable thermodynamic equilibrium as exemplified by thermoelastic buckling [10, 14] corresponding to an initial state of minimum entropy. The other is an instability in the vicinity of a steady state of flow as exemplified by buckling of layered viscous solids in compression. Both cases lead to dominant dissipative structures appearing as a dominant wavelength in many examples of viscous and viscoelastic instability of layered media [7, 13] discussed in the context of irreversible thermodynamics.

2. Principle of virtual dissipation in nonlinear irreversible thermodynamics. It was shown originally in 1954 [1] and in some subsequent work [2–4] that a general Lagrangian thermodynamics of irreversible processes can be developed by introducing a fundamental *non-classical collective potential.*

$$V = U - T_r S \tag{2.1}$$

where U is the internal energy of the system, S its entropy and T_r the constant temperature of an associated large thermal reservoir which we have called a *thermal well.* The terminology of collective potential for V and thermal well for the isothermal reservoir was introduced in a recent paper [12] where the Lagrangian formulation is developed for nonlinear irreversible thermodynamics based on a *generalization of d'Alembert's principle.* The results are briefly summarized here and in the next section in view of their application to rheology.

In spite of a formal similarity, the collective potential (2.1) should not be confused with the concept of availability which is not a thermodynamic potential but a measure of available energy of a system at uniform temperature. The usefulness of the collective potential is due to several important properties.

One of these is its *additive property.* The thermodynamic system may be composed of a large member of cells each with its own *cell potential*

$$\mathcal{V}_k = \mathcal{U}_k - T_r \mathcal{S}_k \tag{2.2}$$

when $\mathcal{U}_k$ and $\mathcal{S}_k$ are the internal energy and entropy of the cell. The collective potential of the system of cells is

$$V = \sum^{k} \mathcal{V}_k = U - T_r S \tag{2.3}$$

where

$$U = \sum^{k} \mathcal{U}_k \,, \qquad S = \sum^{k} \mathcal{S}_k \;. \tag{2.4}$$

In particular the cells may all be at different temperatures. Thus the collective potential applies to a system with a *non-uniform temperature distribution,* as shown in many applications to thermoelasticity and heat transfer [3, 4, 8, 10, 14].

When a particular cell is at uniform temperature T_k another important property is obtained by considering the state variables of the cell to be its entropy $\mathcal{S}_k$ and a certain number of other variables q_l . We may then write

$$d\mathcal{V}_k = \sum^{l} \frac{\partial \mathcal{U}}{\partial q_l} \, dq_l + \frac{\partial \mathcal{U}_k}{\partial \mathcal{S}_k} \, d\mathcal{S}_k - T_r \, d\mathcal{S}_k \, . \tag{2.5}$$

From the classical relations

$$\partial \mathcal{U}/\partial \mathcal{S}_k = T_k \tag{2.6}$$

we derive

$$d\mathcal{V}_k = \sum^{l} \frac{\partial \mathcal{U}}{\partial q_l} \, dq_l + \theta_k \, d\mathcal{S}_k \tag{2.7}$$

where

$$\theta_k = T_k - T_r \tag{2.8}$$

is the excess temperature above the thermal well. Finally we derive

$$\theta_k = \partial \mathcal{V}_k / \partial \mathcal{S}_k \, . \tag{2.9}$$

A third important property is obtained from conservation of energy. Assume that the system exchanges thermal energy only with the thermal well. Denote by H_r the thermal energy thus acquired by the thermal well. Energy conservation requires

$$dU = dW - dH_r \tag{2.10}$$

where dW is the work of the externally applied forces. We may also write

$$S' = S + (H_r/T_r) \tag{2.11}$$

where S' is the total entropy of the hypersystem composed of the thermal well, and the *primary system* of internal energy U and entropy S. From Eqs. (2.1), (2.10) and (2.11) we derive

$$dV - dW = -T_r dS'. \tag{2.12}$$

In this relation the differentials are to be considered as variations in the vicinity of a *frozen configuration at a given instant.* The relation is valid for all transformations *whether reversible or not.* Consider the system to be defined by a number of generalized state variables q_i and assume that they are given variations satisfying suitable conservation and mechanical constraints. Eq. (2.12) may then be written as a variational principle

$$\delta V - \delta W = -T_r \delta S'. \tag{2.13}$$

By d'Alembert's principle we may also write

$$\delta W = \sum^{i} Q_i \, \delta q_i - \sum^{i} I_i \, \delta q_i \tag{2.14}$$

where Q_i are the generalized applied forces while $-I_i$ are the reversed frozen inertia forces at the particular instant considered. The variational principle (2.13) thus becomes

$$\delta V + \sum^{i} I_i \, \delta q_i - \sum^{i} Q_i \, \delta q_i + T_r \, \delta S' = 0. \tag{2.15}$$

We have called it the *principle of virtual relative dissipation* [12].

An alternate form of the principle is obtained by considering a collection of cells and the entropy of each cell $\mathcal{S}_k$ to be composed of two terms

$$\mathcal{S}_k = s_k + s_k^*, \tag{2.16}$$

where s_k is the entropy *supplied to* the cells and s_k^* is the entropy *produced by* the cell. Since S' is the total entropy generated in the hypersystem an obvious property is

$$S' = \sum^{k} s_k^*. \tag{2.17}$$

Hence (2.15) is written

$$\delta V + \sum^{i} I_i \, \delta q_i - Q_i \, \delta q_i + T_r \sum^{k} \delta s_k^* = 0. \tag{2.18}$$

On the other hand,

$$\delta V = \sum^{k} \left[\frac{\partial \mathcal{V}_k}{\partial q_l} \, \delta q_l + \frac{\partial \mathcal{V}_k}{\partial \mathcal{S}_k} \, \delta(s_k + s_k^*) \right] \cdot \tag{2.19}$$

Substituting this value into Eq. (2.18) and using relation (2.9), we obtain

$$\delta_R V + \sum^{i} I_i \, \delta q_i - \sum^{i} Q_i \, \delta q_i + \sum^{k} T_k \, \delta s_k^* = 0, \tag{2.20}$$

where δ_R denotes a restricted variation obtained by excluding the variation δs_k^* of the produced entropy. We have called (2.20) the *principle of virtual intrinsic dissipation* [12].

The physical reason for these two forms of dissipation follows from a distinction between a relative dissipation rate $T_r \dot{s}_k^*$ and an intrinsic dissipation rate $T_k \dot{s}_k^*$ where $\dot{s}_k^*$ is the rate of entropy production which has been discussed in more detail earlier [12]. The quantity $T_k \dot{s}_k^*$ is the heat produced at the temperature T_k . It is not entirely lost in the presence of a thermal well at a lower temperature T_r , since some of it may be transformed into work equal to $\theta_k \dot{s}_k^* = (T_k - T_r) \dot{s}_k^*$ by a Carnot cycle. Note that the total relative dissipation is proportional to the total rate of entropy production S' of the hypersystem, namely

$$\sum^{k} T_r \dot{s}_k^* = T_r \dot{S}'. \tag{2.21}$$

We have defined generalized dissipative forces X_i by writing

$$\sum^{i} X_i \, \delta q_i = \sum^{k} T_k \, \delta s_k^*. \tag{2.22}$$

They are *frozen* dissipative forces for a given state of the system at a given instant. In terms of dissipative forces the principle of virtual dissipation is written

$$\delta_R V + \sum^{i} I_i \, \delta q_i - \sum^{i} Q_i \, \delta q_i + \sum^{i} X_i \, \delta q_i = 0. \tag{2.23}$$

Integrated with respect to time it acquires a Hamiltonian form

$$\int_0^t \left[\delta_R V + \sum^i I_i \, \delta q_i + \sum^i X_i \, \delta q_i - \sum^i Q_i \, \delta q_i \right] dt = 0. \tag{2.24}$$

However, nothing essentially new is added by writing it in this form, whose main interest is to provide an immediate derivation of expression (2.29) below for the inertia forces.

Finally it should be pointed out that a complete physical description requires a knowledge of the frozen dissipative forces in terms of the state of the system q_i and the velocities $\dot{q}_i$. This is expressed by *rate equations*

$$X_i = R_i(q_i \, , \dot{q}_i) \tag{2.25}$$

with the basic inequality

$$\sum^i R_i \dot{q}_i \geq 0. \tag{2.26}$$

If some of the mechanical forces Q_i are derived from a potential G we introduce a *mixed collective potential*

$$\mathcal{P} = V + G \tag{2.27}$$

The principle of virtual dissipation (2.23) then becomes

$$\delta_R \mathcal{P} + \sum^i I_i \, \delta q_i + \sum^i X_i \, \delta q_i - \sum^i Q_i \, \delta q_i = 0. \tag{2.28}$$

For example, G may represent a gravity or an electrostatic potential.

The system will be called *holonomic* in a generalized thermodynamic sense if the variations δq_i are arbitrary while respecting at the same time not only the mechanical constraints but basic conservation constraints of mass energy and electric charge.

For such a holonomic system, a well-known classical derivation in terms of the kinetic energy $\mathfrak{T}$ yields the following expression for the inertia forces

$$I_i = \frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathfrak{T}}{\partial q_i} \tag{2.29}$$

The variational principle (2.28) then leads immediately to *Lagrangian type equations*

$$\frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathfrak{T}}{\partial q_i} + \frac{\partial \mathcal{P}}{\partial q_i} + R_i = Q_i \tag{2.30}$$

for the generalized coordinates.

Principle of virtual thermodynamic equilibrium. The variational principle (2.15) may be interpreted in a different way by defining relative dissipative forces X_i' putting

$$T_r \, \delta S' = \sum^i X_i' \, \delta q_i \tag{2.31}$$

We then replace Q_i by $Q_i - X_i'$ in Eq. (2.15). This yields

$$\delta V + \sum^i I_i \, \delta q_i - \sum^i Q_i \, \delta q_i + \sum^i X_i' \, \delta q_i = -T_r \, \delta S_v' \tag{2.32}$$

where $\delta S_v'$ is the virtual change of entropy for a system subject to forces Q_i; reverse inertia forces $-I_i$ and *reverse dissipative forces* $-X_i'$. Putting $\delta S_v' = 0$ leads to the variational principle (2.15); this amounts to stating that by *reversing* the dissipative forces the system is in *virtual thermodynamic equilibrium.*

Isothermal and quasi-isothermal systems. For an isothermal system at the uniform constant temperature T_r of the thermal well, the collective potential coincides with the classical Helmholtz free energy.

Note that for a system of cells, we may integrate Eqs. (2.7) first for $\theta_k = 0$ and then for $dq_l = 0$. This yields for the cell potential

$$\mathcal{V}_k = \mathcal{V}_k^{(r)} + \int_0^{\theta_k} \theta_k \, d\mathcal{S}_k , \tag{2.33}$$

where $\mathcal{V}_k^{(r)}$ is the Helmholtz free energy of the cell at the temperature T_r while the integral is evaluated for constant values q_l . When θ_k is small, i.e. for a *quasi-isothermal* system, expression (2.33) becomes

$$\mathcal{V}_k = \mathcal{V}_k^{(r)} + \tfrac{1}{2}(c_k\theta_k^2/T_r) \tag{2.34}$$

where c_k is the heat capacity of the cell at the temperature T_r . It remains a function of q_l . The case of nonlinear quasi-isothermal thermoelasticity was developed in detail earlier [10].

3. Nonlinear quasi-reversible systems and Onsager's principle.

D'Alembert's principle may be interpreted in a more fundamental thermodynamic context. When reverse relative dissipative and inertia forces are applied, the instantaneous state of the system is one of both mechanical and thermodynamic virtual equilibrium. If the actual dissipative forces X_i' are now applied to this system its equilibrium is disturbed. In particular, if the actual transformations are quasi-reversible, the disturbance of the virtual equilibrium by the dissipative forces may be assumed small and, as pointed out earlier [12], Onsager's principle becomes applicable [15–18].

For a system of cells, at different temperatures, we may express Onsager's principle for a cell in the form

$$T_k \, \delta s_k^* = \frac{\partial D_k}{\partial \dot{q}_l} \, \delta q_l \tag{3.1}$$

where q_l are the cell coordinates while

$$D_k = \frac{1}{2} \sum^{lm} b_{lm} \dot{q}_l \dot{q}_m = \tfrac{1}{2} T_k \dot{s}_k^* \tag{3.2}$$

is the dissipation function of the cell and $\dot{s}_k^*$ its rate of entropy production. It is easy to show [12] that for generalized coordinates q_i for the total system we may write

$$\sum^{k} T_k \, \delta s_k^* = \sum^{i} \frac{\partial D}{\partial \dot{q}_i} \, \delta q_i \tag{3.3}$$

with the total dissipation function

$$D = \sum^{k} D_k = \frac{1}{2} \sum^{ij} b_{ij} \dot{q}_i \dot{q}_j \, . \tag{3.4}$$

In these expressions b_{lm} and b_{ij} are functions respectively of q_l and q_i . By definition it follows from (3.4) that the generalized intrinsic dissipative force is

$$X_i = \partial D/\partial_i \dot{q} \, . \tag{3.5}$$

This form of Onsager's principle has been used extensively by the author in earlier work.

Minimum dissipation. A principle of *instantaneous* minimum dissipation already formulated earlier [2] in a more restricted context may be stated as follows [12]. Consider the system in its instantaneous frozen state, the direction of the velocity vector $\dot{q}_i$ is given by the minimum principle

$$D = \text{minimum} \tag{3.6}$$

when only the velocities $\dot{q}_i$ are varied while obeying the constraint

$$\sum^{i} X_i q_i = \text{constant} \tag{3.7}$$

This principle is a consequence of Eq. (3.1). If the system is holonomic the frozen values of X_i are

$$X_i = -\frac{\partial \mathcal{P}}{\partial q_i} - I_i + Q_i \, . \tag{3.8}$$

These are expressed in terms of the applied forces Q_i and the instantaneous state and acceleration field of the system. For an isothermal of quasi-isothermal system we may write

$$2D = \sum^{k} (T_r + \theta_k)\dot{s}_k{}^* \cong T_r \sum^{k} \dot{s}_k{}^* = T_r \dot{S}' \tag{3.9}$$

Hence in this case the minimum dissipation principle becomes a *minimum rate of entropy production* principle

$$\dot{S}' = \text{minimum.} \tag{3.10}$$

In particular this is the case for linear systems [2–4].

Lagrangian equations. If the system is holonomic and quasi-reversible the Lagrangian equations (2.30) are formulated in terms of a dissipation function. They become

$$\frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathfrak{T}}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \, . \tag{3.11}$$

The thermodynamics is contained in D by means of entropy production rates and in $\mathcal{P}$ as a mixed thermodynamic and mechanical collective potential.

4. Nonlinear thermo-viscoelasticity; stress-strain relations. We propose to call "viscoelastic" a rheological system which is quasi-reversible from the thermodynamic viewpoint, as described in the preceding section. Hence the dissipative forces are linear functions of the rates $\dot{q}_i$ while the coefficients may be nonlinear functions of the state variables q_i . This distinguishes viscoelasticity from plasticity where the dissipative forces are not linear functions of the rates. We shall derive the stress-strain relations using the concept of *internal coordinates* introduced earlier in the context of linear viscoelasticity [1].

A first step in this direction was accomplished by Schapery [11]. This type of approach is fundamentally different from the work of Coleman [19].

Finite strain of a unit element. In order to establish the stress-strain relations it is sufficient to consider a homogeneous deformation of a *unit element,* i.e. a sample of material which is initially a cube of unit size. The original coordinates x_i become

$$\xi_i = x_i + u_i \tag{4.1}$$

after deformation. The summation convention for dummy indices will be used hereafter. The linear relations

$$u_i = \epsilon_{ij} x_j \tag{4.2}$$

with

$$\epsilon_{ij} = \epsilon_{ji} \tag{4.3}$$

define six Cartesian components of finite strain [7]. However, as already pointed out and illustrated [7, 10], other Cartesian definitions may be used by introducing three relations different from (4.3) in order to eliminate the solid rotation which is included in the nine coefficients ϵ_{ij} .

The present analysis may also be done in terms of non-Cartesian definitions of finite strain using the classical Green's tensor. For simplicity we shall restrict ourselves to the particular definitions (4.2), (4.3).

The corresponding stress components are defined by the virtual work principle

$$\delta W = \tau_{ij}\, \delta\epsilon_{ij} \tag{4.4}$$

where $\tau_{ij} = \tau_{ji}$ and δW is the virtual work of the forces τ_{ij} acting on the faces of the unit element.

Internal and external coordinates. The unit element is defined thermodynamically by the six strain components ϵ_{ij} , its entropy $\mathcal{S}$, and a large number of internal coordinates q_k . The variables ϵ_{ij} may be called external. However, the entropy variable $\mathcal{S}$ is of a special nature, since it may be written as

$$\mathcal{S} = s + s_v^* \tag{4.5}$$

where s is the *entropy supplied* reversibly to the unit element by heating from the outside while s_v^* is the *entropy produced* by the irreversibility. Hence s may be considered as an external variable while the entropy produced s_v^* may be considered as an internal non-holonomic variable.

Stress-strain relations. These relations will be derived in a very general form where both the stresses τ_{ij} and the excess temperature θ will be considered as arbitrary forces applied to the element. The response of the element to these forces are the external coordinates represented by the six strain components ϵ_{ij} and the entropy s supplied to the element. The differential heat energy supplied is $T ds$ where $T = \theta + T_r$ is the temperature of the element.

The cell potential of the unit element is

$$\mathcal{V} = \mathcal{V}(\epsilon_{ij} , \mathcal{S}, q_k) \tag{4.6}$$

It is a function of ϵ_{ij} , $\mathcal{S} = s + s_v^*$ and a large number of internal coordinates q_k .

The intrinsic dissipation rate of the unit element is

$$T\dot{s}_v^* = 2\mathfrak{D}_v = 2\mathfrak{D}_v(\epsilon_{ij} , \dot{\epsilon}_{ij} , \mathcal{S}, q_k , \dot{q}_k). \tag{4.7}$$

Since we have assumed the viscoelastic material to be quasi-reversible by definition, the dissipation function $\mathcal{D}_v$ is a quadratic function of $\dot{\epsilon}_{ij}$ and $\dot{q}_k$ with coefficients dependent on ϵ_{ij}, $\mathcal{S}$ and q_k. The dissipative forces are

$$X_{ij} = \partial \mathcal{D}_v / \partial \dot{\epsilon}_{ij} , \tag{4.8}$$

$$X_k = \partial \mathcal{D}_v / \partial \dot{q}_k . \tag{4.9}$$

We shall apply the virtual intrinsic dissipation principle (2.23) (applying only variations $\delta\epsilon_{ij}$ and δq_k since δs, being independent, may be put equal to zero). We obtain

$$\frac{\partial \mathcal{V}}{\partial \epsilon_{ij}} \delta\epsilon_{ij} + \frac{\partial \mathcal{V}}{\partial q_k} \delta q_k + X_{ij}\, \delta\epsilon_{ij} + X_k\, \delta q_k - \tau_{ij}\, \delta\epsilon_{ij} = 0. \tag{4.10}$$

Since ϵ_{ij}, q_k are holonomic variables they may be varied arbitrarily. This leads to the six equations

$$\tau_{ij} = \frac{\partial \mathcal{V}}{\partial \epsilon_{ij}} + \frac{\partial \mathcal{D}_v}{\partial \dot{\epsilon}_{ij}}. \tag{4.11}$$

A seventh equation is derived from relation (2.9):

$$\theta = \partial \mathcal{V} / \partial s \tag{4.12}$$

In addition, by cancelling the coefficients of δq_k in (4.10) we obtain a large number of equations

$$\frac{\partial \mathcal{V}}{\partial q_k} + \frac{\partial \mathcal{D}_v}{\partial \dot{q}_k} = 0 \tag{4.13}$$

associated with the internal coordinates q_k. Eqs. (4.13) govern the time history of the internal coordinates in terms of ϵ_{ij} and $\mathcal{S}$. They are linear in $\dot{q}_k$. The values of q_k and $\dot{q}_k$ are determined from these equations as functionals of $\epsilon_{ij}(t)$ and $\mathcal{S}(t)$

$$q_k = \mathcal{F}_k[\epsilon_{ij}(t), \mathcal{S}(t)] \qquad \dot{q}_k = \mathcal{G}_k[\epsilon_{ij}(t), \mathcal{S}(t)]. \tag{4.14}$$

The nature of these functionals is strongly conditioned by the positive-definite character of $\mathcal{V}$ and $\mathcal{D}_v$. From Eqs. (4.11) and (4.12) we obtain

$$\begin{aligned} \tau_{ij} &= \frac{\partial}{\partial \epsilon_{ij}} \mathcal{V}(\epsilon_{lm}, \mathcal{S}, \mathcal{F}_k) + \frac{\partial}{\partial \dot{\epsilon}_{ij}} \mathcal{D}_v(\epsilon_{lm}, \dot{\epsilon}_{lm}, \mathcal{S}, \mathcal{F}_k, \mathcal{G}_k), \\ \theta &= \frac{\partial}{\partial s} \mathcal{V}(\epsilon_{lm}, \mathcal{S}, \mathcal{F}_k). \end{aligned} \tag{4.15}$$

These relations are the thermodynamic stress-strain relations in terms of heredity functionals of ϵ_{ij} and $\mathcal{S}$. Note that according to Eq. (4.5) $\mathcal{S} = s + s_v^*$. If the supplied entropy s and the strain ϵ_{ij} are given we may still determine s_v^* by the additional equations (4.7). In many cases we may assume that the entropy produced, s_v^*, does not contribute substantially to the state variable $\mathcal{S}$. This amounts to writing approximately

$$\mathcal{S} = s, \tag{4.16}$$

considering the system as quasi-holonomic. In such a case Eqs. (4.15) express τ_{ij} and θ as functionals of the strain history $\epsilon_{ij}(t)$ and the supplied entropy history $s(t)$. In practice this assumption (4.16) may be introduced as a first approximation. In a second approximation s^* is determined as a function of time by Eq. (4.7).

A case of particular interest is that of a quasi-holonomic system while at the same time $\mathcal{V}$ and $\mathcal{D}_v$ are of the form

$$\begin{aligned} \mathcal{V} &= \mathcal{V}_1(\epsilon_{ij}, s) + \sum^{k} A_k(\epsilon_{ij}, s) q_k + \frac{1}{2} \sum^{lk} a_{lk} q_l q_k , \\ \mathcal{D}_v &= \mathcal{D}_1(\epsilon_{ij}, s, \dot{\epsilon}_{ij}) + \sum^{k} B_k(\epsilon_{ij}, s, \dot{\epsilon}_{ij}) \dot{q}_k + \frac{1}{2} \sum^{lk} b_{lk} \dot{q}_l \dot{q}_k \end{aligned} \tag{4.17}$$

where a_{lk} and b_{lk} are constants. Eqs. (4.13) become

$$\sum^{k} a_{lk} q_k + \sum^{k} b_{lk} \dot{q}_k = \mathcal{A}_l = -A_l - B_l . \tag{4.18}$$

Applying a fundamental solution of these equations derived in linear thermodynamics [1, 2, 4] (see also Sec. 6 below), we obtain the explicit linear functionals

$$\begin{aligned} q_k &= \mathcal{F}_k = \sum^{sl} C_{kl}^{(s)} \int_0^t \exp\,[\lambda_s(t' - t)] \mathcal{A}_l \, dt, \\ \dot{q}_k &= \mathcal{G}_k = \dot{\mathcal{F}}_k \end{aligned} \tag{4.19}$$

where λ_s are non-negative internal relaxation constants and $C_{kl}^{(s)} = C_{lk}^{(s)}$ are non-negative matrices. This type of result was also discussed in the context of the nonlinear mechanics of porous solids [9].

5. Field and Lagrangian equations for a nonlinear thermoviscoelastic continuum. It is worth pointing out that thermodynamic field and Lagrangian equations of a nonlinear viscoelastic continuum may be derived directly from the virtual dissipation principle without a priori knowledge of the physical differential equations which govern the system.

We shall first recall briefly the Cartesian description of the finite deformation of the continuum. The material displacements u_i are expressed as function of time and the initial coordinates x_i :

$$u_i = u_i(x_k , t). \tag{5.1}$$

In a small domain around a material point the differential transformation is

$$du_i = a_{ij} dx_j \tag{5.2}$$

where

$$a_{ij} = \partial u_i / \partial x_j . \tag{5.3}$$

We consider the local transformation

$$du_i = \epsilon_{ij} dx_j \tag{5.4}$$

with $\epsilon_{ij} = \epsilon_{ji}$ such that the two transformations (5.2) and (5.4) differ only by a solid rotation. The Cartesian finite strain is represented by the six components ϵ_{ij} and the associated stress τ_{ij} is defined by the virtual work equation (4.4). This has been discussed extensively elsewhere [7, 10] as have other alternative definitions. Actually we are not restricted to the particular choice (5.4), and the analysis presented here is easily repeated with other measures of strain, including Green's tensor. It will be assumed that ϵ_{ij}

may be expressed in terms of a_{ij}. A useful expression valid to the second order derived by the author in 1939 (see [7]) is

$$\epsilon_{ij} = e_{ij} + \tfrac{1}{2}(e_{kj}\omega_{ki} + e_{ki}\omega_{kj} + \omega_{ki}\omega_{kj}) \tag{5.5}$$

where

$$e_{ij} = \tfrac{1}{2}(a_{ij} + a_{ji}), \qquad \omega_{ij} = \tfrac{1}{2}(a_{ij} - a_{ji}). \tag{5.6}$$

Field equations of nonlinear viscoelasticity. In the preceding section the stress-strain relations were derived for a unit element. The field equations for a nonlinear thermoviscoelastic continuum undergoing non-homogeneous deformations and heat conduction may be derived from the same general principles. The continuum is considered as a collection of infinitesimal cells. The collective potential of the continuum is then

$$V = \int_\Omega \mathcal{V}\, d\Omega \tag{5.7}$$

where Ω is the initial space defined by the initial coordinates x_i, and $d\Omega = dx_1dx_2dx_3$ is the element of initial volume. The cell potential $\mathcal{V}$ of the unit element is

$$\mathcal{V} = \mathcal{V}(\epsilon_{ij}, \mathcal{S}, q_k, x_l) \tag{5.8}$$

It is analogous to (4.6) except for an additional dependence on the initial location x_l.

The local entropy production $\dot{s}^*$ in the present case is composed of two distinct terms. We write for the local intrinsic dissipation of the unit element

$$T\dot{s}^* = 2\mathfrak{D}_v + 2\mathfrak{D}_T \tag{5.9}$$

where

$$\begin{aligned} 2\mathfrak{D}_v &= 2\mathfrak{D}_v(\epsilon_{ij}, \dot{\epsilon}_{ij}, \mathcal{S}, q_k, \dot{q}_k, x_l), \\ 2\mathfrak{D}_T &= T\lambda_{ij}\dot{S}_i\dot{S}_j, \end{aligned} \tag{5.10}$$

and T is the local temperature [10] [11].

The value of $\mathfrak{D}_v$ is the dissipation function due to the viscoelasticity. It is the same as (4.7) except of an additional dependence on the initial coordinates x_i. The entropy production due to heat conduction generates the intrinsic dissipation $\mathfrak{D}_T$. The coefficients $\lambda_{ij} = \lambda_{ji}$ represent the thermal resistivity tensor. It depends on the deformation ϵ_{ij}, the local entropy $\mathcal{S}$, the internal coordinates q_k and the location x_i. We write

$$\lambda_{ij} = \lambda_{ij}(\epsilon_{ij}, \mathcal{S}, q_k, xl). \tag{5.11}$$

We also write

$$T = T(\epsilon_{ij}, \mathcal{S}, q_k, x_l). \tag{5.12}$$

The vector S_i is *the entropy displacement,* a term already introduced earlier [3, 4, 10]. It is defined by writing the rate of entropy flow as

$$\dot{S}_i = \dot{H}_i/T \tag{5.13}$$

where $\dot{H}_i$ is the rate of thermal flow across an area initially equal to unity and initially normal to the x_i axis. The value of $\mathfrak{D}_T$ has been derived and discussed extensively earlier [10].

An important property of S_i is represented by the following relations. The total local entropy of the unit element is

$$\mathcal{S} = s + s^* \tag{5.14}$$

where

$$s = -\partial S_i/\partial x_i \tag{5.15}$$

is the local *entropy supplied,* while s^* is the local entropy produced as defined by Eqs. (5.9).

It should be pointed that in $\mathfrak{D}_v$ and $\mathfrak{D}_T$ the rate variables $\dot{S}_i$ are uncoupled to either $\dot{\epsilon}_{ij}$ or $\dot{q}_k$. Otherwise cross-products would be present such that a sign reversal of $\dot{S}_i$ would generate a change in entropy production. However, this must be excluded because of physical symmetry invariance. The variables defining the system are the fields u_i , S_i of material and entropy displacements, the entropy produced s^*, and the internal coordinates q_k .

We now apply the principle of virtual dissipation (2.23) by varying only the variables u_i and S_i *inside the domain* Ω. The dissipative forces associated with ϵ_{ij} and S_i are

$$\begin{aligned} X_{ij} &= \partial \mathfrak{D}_v/\partial \dot{\epsilon}_{ij} , \\ X_i &= \partial \mathfrak{D}_T/\partial \dot{S}_i = T\lambda_{ij}\dot{S}_j . \end{aligned} \tag{5.16}$$

The variational principle (2.23) applied to the whole continuum now becomes

$$\int_\Omega (\delta_R \mathcal{V} + \rho\ddot{u}_i \,\delta u_i + X_{lm}\,\delta\epsilon_{lm} + X_i\,\delta S_i - \rho\mathcal{B}_i\,\delta u_i)\,d\Omega \tag{5.17}$$

where $\mathcal{B}_i$ is the body force per unit mass and ρ is the initial mass density. We may write

$$\delta_R \mathcal{V} + X_{lm}\,\delta\epsilon_{lm} = \left(\frac{\partial \mathcal{V}}{\partial \epsilon_{lm}} + \frac{\partial \mathfrak{D}_v}{\partial \dot{\epsilon}_{lm}}\right)\delta\epsilon_{lm} + \frac{\partial \mathcal{V}}{\partial s}\,\delta s \tag{5.18}$$

or

$$\delta_R \mathcal{V} + X_{lm}\,\delta\epsilon_{lm} = \tau_{lm}\frac{\partial \epsilon_{lm}}{\partial a_{ij}}\,\delta a_{ij} + \theta\,\delta s. \tag{5.19}$$

This result is obtained by using Eqs. (4.11) and (4.12). We now introduce expression (5.19) into the variational principle (5.17) and integrate by parts taking into account the *holonomic* constraints (5.3) and (5.15) of continuity and conservation, namely

$$a_{ij} = \partial u_i/\partial x_j , \qquad s = -\partial S_i/\partial x_i . \tag{5.20}$$

This yields an expression with arbitrary variations δu_i and δS_i whose coefficients must vanish. As a consequence we obtain six field equations for u_i and S_i :

$$\begin{aligned} \frac{\partial}{\partial x_j}\left(\tau_{lm}\frac{\partial \epsilon_{lm}}{\partial a_{ij}}\right) + \rho\mathcal{B}_i &= \rho\ddot{u}_i , \\ \partial\theta/\partial x_i &= -T\lambda_{ij}\cancel{S_j} . \end{aligned} \tag{5.21}$$ /S

In addition a seventh equation (5.9) is available for the entropy produced, s^*. Note that the last three of Eqs. (5.21) represent the law of heat conduction. Mechanical and thermodynamic heredity properties are implicit in the field equations (5.21) since the internal coordinates q_k in the values of τ_{ij} and λ_{ij} must be expressed by means of the functionals (4.14).

Lagrangian equations of nonlinear thermoviscoelasticity. If the entropy produced s^* does not contribute significantly to the state variables, the system is quasi-holonomic and we write approximately

$$\mathcal{S} = s. \tag{5.22}$$

In this case the nonlinear thermoviscoelastic continuum is described by the two fields

$$\begin{aligned} u_i &= u_i(q, q_2 \cdots q_n , x_l , t), \\ S_i &= S_i(q_1, q_2 \cdots q_n , x_l , t) \end{aligned} \tag{5.23}$$

with generalized coordinates q_i . In addition, the local internal coordinates q_k are given by the functionals (4.14) in terms of the fields u_i and S_i . In this case it is possible to derive Lagrangian-type equations for the continuum.

Following earlier procedure, we consider temperatures to be "applied" at the boundary A as thermal forces dependent on location and time. This may be taken into account by adding thermal driving reservoirs at the boundary. These reservoirs are then included in the collective potential, which is written

$$V = \int_\Omega \mathcal{V}\, d\Omega + \int_A \mathcal{V}_T\, dA \tag{5.24}$$

The cell potentials $\mathcal{V}_T$ representing the applied boundary temperatures are evaluated per unit initial area. As a consequence of (2.7) we may write

$$\delta\mathcal{V}_T = \theta n_i \delta S_i \tag{5.25}$$

where n_i is the unit outward normal of the initial boundary. We derive

$$\delta V_R = \int_\Omega \delta\mathcal{V}_R\, d\Omega + \int_A \theta n_i\ \delta S_i\, dA. \tag{5.26}$$

Note that this variation is performed for an instantaneous configuration at a particular instant, so that in the final result θ may be given functions of time.

The total dissipation function of the continuum is

$$D = \int_\Omega (\mathcal{D}_v + \mathcal{D}_T)\, d\Omega. \tag{5.27}$$

The dissipative force associated with the generalized coordinate q_i is

$$X_i^{(a)} = \partial D/\partial \dot{q}_i\ . \tag{5.28}$$

We shall assume that the body forces $\mathcal{B}_i$ per unit mass are derived from a potential ϕ so that

$$\int_\Omega \rho\mathcal{B}_i\ \delta u_i\, d\Omega = \int_\Omega \rho\ \delta\phi\, d\Omega = \delta G \tag{5.29}$$

With these results the variational principle (2.28) with independent variations of q_i is

$$\delta_R\mathcal{P} + I_i\ \delta q_i + X_i^{(a)}\ \delta q_i - \int_A (f_i\ \delta u_i - \theta n_i\ \delta S_i)\, dA = 0 \tag{5.30}$$

where f_i are boundary forces per unit initial area and

$$\mathcal{P} = \int_\Omega \mathcal{V} \, d\Omega + G \tag{5.31}$$

is a *mixed collective potential.* Equating to zero the coefficients of δq_i in the variational principle (5.30) and introducing the values (2.29) and (5.28) for I_i and $X_i^{(q)}$, we obtain

$$\frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathfrak{T}}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \tag{5.32}$$

with generalized thermomechanical forces

$$Q_i = \int_A \left(f_l \frac{\partial u_l}{\partial q_i} - \theta n_l \frac{\partial S_l}{\partial q_i} \right) dA. \tag{5.33}$$

The kinetic energy is

$$\mathfrak{T} = \frac{1}{2} \int_\Omega \rho \dot{u}_i \dot{u}_i \, d\Omega. \tag{5.34}$$

These Lagrangian equations are similar to (3.7) except for the fact that D and $\mathcal{P}$ are *functionals* of q_i since they contain the local internal coordinates q_k which are themselves expressed by the functionals (4.14).

Note that in the case of linear viscoelasticity this type of functional Lagrangian equation was already introduced using integro-differential operators [4, 7].

6. Linear thermodynamics and viscoelasticity. The generalized coordinates q_i may represent linearized perturbations from a thermodynamic state of equilibrium. In this case we may write (with constants m_{ij} , b_{ij} , a_{ij})

$$\mathfrak{T} = \tfrac{1}{2} m_{ij} \dot{q}_i \dot{q}_j \,, \qquad D = \tfrac{1}{2} b_{ij} \dot{q}_i \dot{q}_j \,, \qquad \mathcal{P} = \tfrac{1}{2} a_{ij} q_i q_j \,, \tag{6.1}$$

The Lagrangian equations become [4, 7]

$$m_{ij} \ddot{q}_j + b_{ij} \dot{q}_j + a_{ij} q_j = Q_i \,. \tag{6.2}$$

For linear thermodynamics the auxiliary variable $\dot{s}^*$ due to entropy production is a second-order negligible quantity, and the system is holonomic. Applying Eqs. (6.1) with internal variables q_k and putting $\mathfrak{T} = 0$, it was shown [1, 2, 4] that the external variables q_i and the corresponding driving forces are related by the following equations:

$$q_i = \hat{A}_{ij} Q_j \,, \qquad Q_i = \hat{Z}_{ij} \tag{6.3}$$

where

$$\begin{aligned} \hat{A}_{ij} &= \hat{A}_{ji} = \sum^{s} \frac{C_{ij}^{(s)}}{\lambda_s + p} \,, \\ \hat{Z}_{ij} &= \hat{Z}_{ji} = \sum^{s} \frac{p}{r_s + p} Z_{ij}^{(s)} + Z_{ij} + Z_{ij}' p. \end{aligned} \tag{6.4}$$

These quantities are symmetric operators where $p = d/dt$, λ_s and r_s are non-negative as well as the matrices $C_{ij}^{(s)}$, $Z_{ij}^{(s)}$, Z_{ij} and Z_{ij}'. The significance of the fractional operators is given by

$$\begin{aligned} \frac{1}{p+a} z(t) &= e^{-at} \int_0^t e^{at'} z(t')\, dt', \\ \frac{p}{p+a} z(t) &= e^{-at} \int_0^t e^{at'} \frac{dz}{dt'}\, dt. \end{aligned} \tag{6.5}$$

The operational notation is extremely general and convenient, since relations (6.3) remain valid when q_i and Q_i are proportional to the exponential function of time, exp (pt), where p is either real, complex or pure imaginary $(p = i\omega)$. Thus a single formalism represents instability (p real and positive), harmonic response (p imaginary), and damped natural oscillations (p complex).

A viscoelastic material is a particular case where the stress τ_{ij} and the strain ϵ_{ij} play the role of external driving forces and external coordinates. The stress-strain relations obtained from (6.3) are [1, 2]

$$\tau_{ij} = \hat{Z}_{ij}^{lk} \epsilon_{lk}, \tag{6.6}$$

where

$$\hat{Z}_{ij}{}^{lk} = \hat{Z}_{lk}{}^{ii} = \sum^{s} \frac{p}{r_s + p} Z_{ij}{}^{lk(s)} + Z_{ij}{}^{lk} + Z_{ij}{}^{lk} p. \tag{6.7}$$

There results are extremely general, and provide a basic invariance for compound systems. For example, a composite material where each component satisfies the basic Lagrangian equations (6.1) also satisfies the same Lagrangian equations. Hence the stress-strain relations of the composite retain the invariant form (6.6). The symmetry property $\hat{Z}_{ij} = \hat{Z}_{ji}$ is also invariant for composite systems, thus providing immediately reciprocity relations of a very general type for all thermodynamic and mechanical systems. In particular, these results have been applied to porous media [5], [6], where the stress-strain relations include fluid micro-seepage, thermoelastic and viscoelastic properties, with internal coordinates representing a large category of physical, chemical and electrical phenomena. An outline of the linear thermodynamics of viscoelasticity may also be found in a book by Fung [21].

7. Thermodynamics of plasticity. A fundamental thermodynamic distinction between nonlinear viscoelasticity and plasticity is brought out by assuming the following physical model. We consider again a unit element and assume the medium to obey the laws of linear thermodynamics except at a large number of "slip centers" which are essentially nonlinear. This linear system is characterized by the six strain components ϵ_{ij} and a large number of internal coordinates q_k. These internal coordinates are of a very general nature. They may describe elastic deformation, small dislocation motions, local thermoelastic effects with small temperature changes, small chemical and phase disturbances, thermodiffusion, viscous properties of intercrystalline boundaries, etc. For small perturbations of this type the system described by the coordinates ϵ_{ij} and q_k obeys the general equations of linear thermodynamics obtained earlier [1, 2, 4] and briefly described in the preceding section. In this linear formulation the temperature changes due to entropy production are neglected, but small thermoelastic effects are not. The system is assumed *quasi-isothermal*, all temperatures deviating only slightly from the thermal well temperature.

To the internal coordinates characterizing the linear system we must add others denoted by q_s which describe the motion of the slip centers. However these slip centers are not free to move according to linear laws and they exert a force $-X_s$ on the linear system. By reaction a force X_s is exerted on the slip centers.

Plastic behavior is introduced by assuming a nonlinear relation between the displacement q_s and the force X_s applied to it:

$$q_s = F_s(X_s). \tag{7.1}$$

This relation is not necessarily single-valued, thus allowing for hysteresis. The linear portion of the system behaves as a thermodynamic system subject to the applied forces τ_{ij} and $-X_s$. According to earlier results [1, 2, 4] the behavior of the system is described by the operational relations

$$\tau_{ij} = \hat{Z}_{ij}{}^{\mu\nu}(\# \, \epsilon_{\mu\nu}) + \sum^{s} \hat{Y}_{ij}{}^{s} q_s , \qquad -X_s = \hat{Y}_{ij}{}^{s} \epsilon_{ij} , \tag{7.2}$$

✗

where the operators are

$$\begin{aligned} \hat{Z}_{ij}{}^{\mu\nu} &= \int_0^\infty Z_{ij}{}^{\mu\nu}(r) \frac{p}{p+r} \, dr + Z_{ij}{}^{\mu\nu} + Z_{ij}{}'^{\mu\nu} p, \\ \hat{Y}_{ij}{}^{s} &= \int_0^\infty Y_{ij}{}^{s}(r) \frac{p}{p+r} \, dr + Y_{ij}{}^{s} + Y_{ij}{}'^{s} p. \end{aligned} \tag{7.3}$$

These expressions coincide with those of Eqs. (6.6), (6.7) if the summations are replaced by integrals. The spectral distributions $Z_{ij}{}^{\mu\nu}(r)$ and $Y_{ij}{}^{s}(r)$ are generalized functions. They represent a discrete summation as a particular case if we introduce delta functions.

We now eliminate q_s and X_s between Eqs. (7.1) and (7.2). We derive

$$\tau_{ij} = \hat{Z}_{ij}{}^{\mu\nu} \epsilon_{\mu\nu} + \sum^{s} \hat{Y}_{ij}{}^{s} F_s(-\hat{Y}_{ij}{}^{s} \epsilon_{ij}). \tag{7.4}$$

These general stress-strain relations represent the combined viscoelastic and nonlinear plastic behavior.

Entropy production and variational viewpoints. The result expressed by Eqs. (7.4) may obviously be brought into the unifying framework of the variational principles formulated in the foregoing sections by considering the system to be represented by the following invariants. The cell potential of the unit element is

$$\mathcal{V} = \mathcal{V}(\epsilon_{ij} , q_k , q_s) \tag{7.5}$$

which is a quadratic function of the variables with constant coefficients. The rate of dissipation is

$$T_r \dot{S}' = D(\dot{\epsilon}_{ij} , \dot{q}_k , \dot{q}_s) + X_s \dot{q}_s \tag{7.6}$$

where D is a quadratic function with constant coefficients The entropy production is thus separated into two groups of terms. The group

$$T_r \dot{S}_p = X_s \dot{q}_s \tag{7.7}$$

characterizes separately the dissipation due to plasticity.

The Lagrangian equations are

$$\begin{aligned} \frac{\partial \mathcal{V}}{\partial \epsilon_{ij}} + \frac{\partial D}{\partial \dot{\epsilon}_{ij}} &= \tau_{ij} \\ \frac{\partial \mathcal{V}}{\partial q_k} + \frac{\partial D}{\partial \dot{q}_k} &= 0 \\ \frac{\partial D}{\partial \dot{q}_s} &= -X_s \end{aligned} \tag{7.8}$$

This is a linear system with internal coordinates q_k implying the operational relations (7.2).

Strain-hardening. If we assume that the number of slip centers diminishes as the deformation progresses, the material will exhibit strain-hardening. This amounts to saying that a particular slip q_s cannot progress above a certain value beyond which it remains constant. This may be expressed by introducing functions $F_s(X_s)$ which have a limiting constant value beyond a certain magnitude. Other physical types of strain-hardening may be taken into account by similar procedures.

Materials with internal failure. Composite materials with fiber components may exhibit irreversible behavior due to gradual breaking of the fibers. Granular materials may also exhibit a similar behavior due to gradual failure or extension of microcracks. Such behavior may be included here by assuming that the local forces X_s drop to zero in increasing number once they reach a certain value. The stress-strain relations are then of the same form as (7.4).

It should be noted that in crack propagation the energy dissipated is not necessarily transformed into heat locally. Actually it may simply become non-retrievable by acoustic radiation. Furthermore, in accordance with the Griffith theory of brittle fracture, it may be transformed into non-retrievable surface energy in the form of surface tension. Although this is not actually an entropy production in the true thermodynamic sense, the formulation retains the form of a dissipation of energy.

8. Nonlinear thermoelasticity and heat conduction. A purely elastic medium deforms with associated temperature changes and consequently generates entropy through heat conduction. In addition to an earlier linear treatment [3, 4], the quasi-isothermal nonlinear case was discussed extensively elsewhere [10]. A general nonlinear analysis derived from the variational principle (2.23) was also developed in a recent publication [12] and is outlined hereafter. This approach to nonlinear thermoelasticity differs fundamentally from the work of other investigators [22–24] derived from classical concepts.

Essentially the results may be obtained from the case of viscoelasticity analyzed in Sec. 5 by putting equal to zero $\mathfrak{D}_i$ and the internal variables q_k. The cell potential of the unit element is

$$\mathcal{V} = \mathcal{V}(\epsilon_{ij}, \mathcal{S}, x_l). \tag{8.1}$$

The elastic continuum is described by the material displacement u_i, the entropy displacement S_i and the entropy produced s^*. The local entropy is

$$\mathcal{S} = s + s^* \tag{8.2}$$

where

$$s = -\partial S_i/\partial x_i \, . \tag{8.3}$$

is the entropy supplied. The collective potential of the elastic continuum is

$$V = \int_\Omega \mathcal{V} \, d\Omega. \tag{8.4}$$

The term *thermoelastic potential* was introduced earlier [3, 4, 10] to designate this potential. In accordance with (5.10) the local intrinsic rate of dissipation is

$$T\dot{s}^* = 2\mathcal{D}_T = T\lambda_{ij}\dot{S}_i\dot{S}_j \tag{8.5}$$

where

$$T = T(\epsilon_{ij} \, , \mathcal{S}, x_l), \tag{8.6}$$

$$\lambda_{ij} = \lambda_{ji} = \lambda_{ij}(\epsilon_{ij} \, , \mathcal{S}, x_l) \tag{8.7}$$

are respectively the local temperature and the thermal resistivity as defined in Sec. 5. Hence the dissipative force associated with S_i is

$$X_i = \partial\mathcal{D}_T/\partial\dot{S}_i = T\lambda_{ij}\dot{S}_j \tag{8.8}$$

The variational principle (2.23) for arbitrary variations $\delta u_i \delta S_i$ inside the continuum Ω is expressed by

$$\int_\Omega (\delta_R\mathcal{V} + \rho\ddot{u}_i \, \delta u_i + X_i \, \delta S_i - \rho\mathcal{B}_i \, \delta u_i) \, d\Omega = 0 \tag{8.9}$$

where $\mathcal{B}_i$ are body forces per unit mass and ρ is the initial mass density. We write

$$\delta_R\mathcal{V} = \frac{\partial\mathcal{V}}{\partial\epsilon_{lm}} \, \delta\epsilon_{lm} + \frac{\partial\mathcal{V}}{\partial s} \, \delta s. \tag{8.10}$$

or

$$\delta_R\mathcal{V} = \tau_{lm} \frac{\partial\epsilon_{lm}}{\partial a_{ij}} \, \delta a_{ij} + \theta \, \delta s. \tag{8.11}$$

with

$$\tau_{lm} = \partial\mathcal{V}/\partial\epsilon_{lm} \, , \qquad \theta = \partial\mathcal{V}/\partial s. \tag{8.12}$$

These equations are the thermodynamic stress-strain relations.

We substitute the value (8.11) of $\delta_R\mathcal{V}$ in the variational principle (8.9) and integrate by parts, using the values (5.3) and (8.3) for a_{ij} and s. Putting equal to zero the coefficients of δu_i and δS_i yields the field equations

$$\begin{gathered} \frac{\partial}{\partial x_j}\left(\tau_{lm} \frac{\partial\epsilon_{lm}}{\partial a_{ij}}\right) + \rho\mathcal{B}_i = \rho\ddot{u}_i \, , \\ \frac{\partial\theta}{\partial x_i} + T\lambda_{ij}\dot{S}_j = 0. \end{gathered} \tag{8.13}$$

To these six equations we must add Eq. (8.5) for $\dot{s}^*$. Thus we have seven equations for the seven variables u_i , S_i and s^*.

The stress-strain relations (8.12), as already shown in a more restricted context [3, 4, 10], may be expressed differently by writing (8.10) as

$$d\mathcal{V} = \tau_{ij} d\epsilon_{ij} + \theta ds. \tag{8.14}$$

This being an exact differential, we may integrate $d\mathcal{V}$ along a path $\theta = 0$, then maintaining constant the deformation ϵ_{ij} we vary only θ. This yields

$$\mathcal{V} = \mathcal{V}_r(\epsilon_{ij}) + \int_0^\theta \theta(\epsilon_{ij})\, ds \tag{8.15}$$

where $\mathcal{V}_r$ is the classical isothermal free energy for $\theta = 0$. The stress is

$$\tau_{ij} = \bar{\tau}_{ij} + \int_0^\theta \frac{\partial \theta}{\partial \epsilon_{ij}}\, ds \tag{8.16}$$

where

$$\bar{\tau}_{ij} = \partial \mathcal{V}_r / \partial \epsilon_{ij} \tag{8.17}$$

are the isothermal stress-strain relations for $\theta = 0$. In particular, for the *quasi-isothermal case* (θ small) already analyzed in detail elsewhere [10] we write

$$\mathcal{V} = \mathcal{V}_r + \frac{1}{2}\frac{c\theta^2}{T_r}. \tag{8.18}$$

where $c(\epsilon_{ij})$ is the heat capacity per unit initial volume at the strain ϵ_{ij}.

Lagrangian equations. If the entropy produced s^* does not contribute significantly to the value of the state variables, we may introduce the quasi-holonomic approximation $s = \mathcal{S}$. The fields u_i and S_i are then expressed in terms of generalized coordinates q_i by Eqs. (5.23). In general they may contain the time t explicitly. However, without restricting the generality we may assume that t does not appear explicitly in these equations. We may then introduce the following expressions.

A collective potential V may be written of variation

$$\delta V = \int_\Omega \delta V(\epsilon_{ij}, s, x_l)\, d\Omega + \int_A \theta n_i\, \delta S_i\, dA \tag{8.19}$$

where the second integral extended to the boundary A is the collective potential of purely thermal cells representing "driving temperatures" at the boundary A. We may write

$$\delta V = \delta V'(q_i) + \int_A \theta n_i\, \delta S_i\, dA. \tag{8.20}$$

The kinetic energy is

$$\mathcal{T} = \frac{1}{2}\int_\Omega \rho \dot{u}_i \dot{u}_i\, d\Omega = \tfrac{1}{2} m_{ij}(q_l)\dot{q}_i\dot{q}_j \tag{8.21}$$

and the dissipation function is

$$D = \frac{1}{2}\int_\Omega T\lambda_{ij}\dot{S}_i\dot{S}_j\, d\Omega = \tfrac{1}{2} b_{ij}(q_l)\dot{q}_i\dot{q}_j\ . \tag{8.22}$$

For body forces derived from a potential ϕ, we also write the mixed collective potential

$$\mathcal{P} = V' + G \tag{8.23}$$

where G is expressed by (5.29).

The Lagrangian equations derived directly from the variational principle (2.28) are written

$$\frac{d}{dt}\left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{T}}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i\ . \tag{8.24}$$

The generalized thermomechanical boundary force Q_i is given by expression (5.33).

Nonlinear heat conduction. The case of pure heat conduction is derived from the preceding analysis by assuming zero deformation ($\epsilon_{ij} = 0$). The variational principle was treated and applied extensively in a sequence of papers originating in 1957 and collected in a monograph [8]. The system is completely described in this case by the heat displacement field H_i . It is therefore holonomic with corresponding Lagrangian equations. The entropy $\mathcal{S}$ and temperature T are determined by

$$h = -\frac{\partial H_i}{\partial x_i} \tag{8.25}$$

which was referred to as the "heat content" [8].

In the present case the variational principle (8.9) is written

$$\int_\Omega (\delta_R \mathcal{V} + T\lambda_{ij}\dot{S}_j\ \delta S_i)\, d\Omega = 0 \tag{8.26}$$

where

$$\delta_R \mathcal{V} = \theta\delta\mathcal{S} = -\theta\frac{\partial}{\partial x_i}\left(\frac{\delta H_i}{T}\right). \tag{8.27}$$

X

Hence (8.26) becomes

$$\int_\Omega \left(\frac{\partial \theta}{\partial x_i} + \lambda_{ij}\dot{H}_j\right)\frac{\delta H_i}{T}\, d\Omega. \tag{8.28}$$

Replacing $\delta H_i/T$ by δH_i , we obtain

$$\int_\Omega (\theta\ \delta h + \lambda_{ij}\dot{H}_j\ \delta H_i)\, d\Omega = 0 \tag{8.29}$$

where the value $\theta = \theta(h)$ is a function of h. By adding thermal cells at the boundary, the term $\theta\delta h$ may be considered to include these cells. This amounts to adding a surface integral at the boundary A. Eq. (8.29) becomes

$$\int_\Omega (\theta\ \delta h + \lambda_{ij}\dot{H}_j\ \delta H_i)\, d\Omega = -\int_A \theta n_k\ \delta H_k\, dA. \tag{8.30}$$

This is the variational principle derived in 1957 by the author (see [8]). The corresponding Lagrangian equations are obtained by writing

$$H_i = H_i(q_1\ , q_2\ , \cdots q_n\ , x_i\ , t) \tag{8.31}$$

in terms of generalized coordinates q_i. They are

$$\frac{\partial V}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} = Q_i \tag{8.32}$$

where

$$V = \int_\Omega d\Omega \int_0^\theta \theta \, dh \tag{8.33}$$

was referred to as the *thermal potential* and

$$Q_i = -\int_A \theta n_k \frac{\partial H_k}{\partial q_i} \, dA \tag{8.34}$$

as the generalized *thermal force*. The *thermal dissipation function* is

$$D = \frac{1}{2} \int_\Omega \lambda_{ij} \dot{H}_i \dot{H}_j \, d\Omega. \tag{8.35}$$

These results were developed and applied extensively in a monograph [8] to the more general subject of heat transfer.

9. Compressible and heat-conducting Newtonian and non-Newtonian viscous fluids.

The principle of virtual dissipation constitutes a powerful tool for deriving field and Lagrangian equations of Newtonian and non-Newtonian fluids either homogeneous or heterogeneous in any coordinate system including the effect of compressibility and heat conduction as well as the heat generated by friction. We shall describe the flow field by material coordinates, where a fluid particle of initial coordinates x_i is displaced as a function of time to a point of coordinates

$$\xi_i = x_i + u_i(x_l, t). \tag{9.1}$$

At the displaced point ξ_i the velocity is

$$\dot{\xi}_i = \dot{u}_i = \frac{\partial \xi_i}{\partial t} \tag{9.2}$$

and the strain rate is

$$e_{ij}' = \frac{1}{2}\left(\frac{\partial \dot{u}_i}{\partial \xi_j} + \frac{\partial \dot{u}_j}{\partial \xi_i}\right). \tag{9.3}$$

As in (5.2) and (5.3), we write

$$d\xi = A_{ij} dx_j, \tag{9.4}$$

where

$$A_{ij} = \partial \xi_i / \partial x_j = \delta_{ij} + a_{ij}, \qquad a_{ij} = \partial u_i / \partial x_j. \tag{9.5}$$

A fluid element of initial volume $d\Omega$ acquires after deformation a volume $\Delta d\Omega$ where

$$\Delta = \det(A_{ij}) = \det(\delta_{ij} + a_{ij}) \tag{9.6}$$

is the Jacobian of the transformation of initial to final coordinates. It represents the volume of an initial unit volume.

In order to apply the variational principle with material coordinates, we need to express the strain rate in terms of initial coordinates. This is easily obtained by writing

$$\frac{\partial \dot{u}_i}{\partial \xi_j} = \frac{\partial \dot{u}_i}{\partial x_k}\frac{\partial x_k}{\partial \xi_j} \tag{9.7}$$

The derivatives $\partial x_j/\partial \xi_k$ are evaluated by solving the linear equations (9.4) for dx_i ; we obtain

$$dx_i = B_{ij} d\xi_j \tag{9.8}$$

where the matrix $[B_{ij}]$ is the inverse of the matrix $[A_{ij}]$. Hence

$$\frac{\partial x_i}{\partial \xi_j} = B_{ij} = \frac{C_{ji}}{\Delta}, \tag{9.9}$$

where C_{ij} is the cofactor of A_{ij} in the determinant Δ. Thus (9.7) becomes

$$\frac{\partial \dot{u}_i}{\partial \xi_j} = \frac{\partial \dot{u}_i}{\partial x_k} B_{kj} = \dot{a}_{ik} B_{kj} \tag{9.10}$$

and the strain-rate (9.3) is

$$e_{ij}' = \tfrac{1}{2}(\dot{a}_{ik} B_{kj} + \dot{a}_{jk} B_{ki}). \tag{9.11}$$

We shall assume the general case of a non-homogeneous fluid. This is taken into account by introducing the initial coordinates in the thermodynamic properties. The temperature of the unit element of fluid is

$$T = T(\Delta, \mathcal{S}, x_i). \tag{9.12}$$

It is a function of its volume Δ, its entropy $\mathcal{S}$ and its initial location x_i . The cell potential of the unit element is also written

$$\mathcal{V} = \mathcal{V}(\Delta, \mathcal{S}, x_i) \tag{9.13}$$

and the collective potential of the fluid is

$$V = \int_\Omega \mathcal{V}(\Delta, \mathcal{S}, x_i)\, d\Omega \tag{9.14}$$

where the entropy is $\mathcal{S} = s + s^*$. We may also obtain quite simply the dissipation due to thermal conduction. The derivation does not depend on the Newtonian or non-Newtonian character of the fluid. We assume that the thermal conductivity k of the fluid in the deformed state remains isotropic. This thermal conductivity k is defined in the conventional way in terms of $\partial\theta/\partial \xi_i$. It is different from the thermal conductivity K_{ij} introduced below and defined in terms of the initial coordinates. The value of k depends only on the change of volume Δ, the entropy $\mathcal{S}$ and the initial coordinate x_i :

$$k = k(\Delta, \mathcal{S}, x_i). \tag{9.15}$$

The rate of entropy production in a unit element of fluid due to conduction is

$$\dot{s}_T^* = \frac{k}{T^2}\frac{\partial \theta}{\partial \xi_l}\frac{\partial \theta}{\partial \xi_l}\Delta. \tag{9.16}$$

The factor which multiplies the volume Δ obviously represents the rate of entropy production in the unit volume measured after deformation. We introduce the coordinate transformation from ξ_i to x_i and (9.16) becomes

$$\dot{s}_T^* = \frac{K_{ij}}{T^2} \frac{\partial \theta}{\partial x_i} \frac{\partial \theta}{\partial x_j} \tag{9.17}$$

with

$$K_{ij} = k \frac{\partial x_i}{\partial \xi_l} \frac{\partial x_j}{\partial \xi_l} \Delta. \tag{9.18}$$

This expression is the thermal conductivity defined for the deformed fluid element in terms of $\partial \theta / \partial x_i$. Note the invariance of this expression under solid rotation, since $(\partial x_i / \partial \xi_l)(\partial x_j / \partial \xi_l)$ is the associated metric tensor of the transformation of ξ_i to x_i. We denote by λ_{ij} the inverse of K_{ij} and put

$$\partial \theta / \partial x_i = -\lambda_{ij} \dot{H}_j . \tag{9.19}$$

With this value (9.17) becomes

$$\dot{s}_T^* = \lambda_{ij} \dot{S}_i \dot{S}_j \tag{9.20}$$

which acquires the same form as previously. Note that λ_{ij} is now anisotropic not because the material has become physically anisotropic but because the local thermal conduction is described in terms of heat flow and thermal gradients in a direction normal to the faces of a deformed element, i.e. a parallelepiped. Hence

$$\lambda_{ij} = \lambda_{ij}(a_{ij}, \mathcal{S}, x_l) \tag{9.21}$$

is now a function of the deformation.

The value of λ_{ij} which is the inverse of K_{ij} is obtained from (9.18) by noting the identity

$$\frac{\partial x_i}{\partial \xi_l} \frac{\partial x_n}{\partial \xi_l} \frac{\partial \xi_m}{\partial x_n} \frac{\partial \xi_m}{\partial x_j} = \delta_{ij} . \tag{9.22}$$

Hence

$$\frac{K_{in}}{k\Delta} \frac{\partial \xi_m}{\partial x_n} \frac{\partial \xi_m}{\partial x_j} = \delta_{ij} \tag{9.23}$$

and

$$\lambda_{ij} = \frac{1}{k\Delta} \frac{\partial \xi_m}{\partial x_i} \frac{\partial \xi_m}{\partial x_j} \tag{9.24}$$

Newtionian fluid. For a Newtonian compressible fluid the intransic rate of dissipation of the unit element due to the viscosity is

$$2\mathfrak{D}_v = T\dot{s}_v^* = \Delta(\lambda e'^2 + 2\eta e_{ij}' e_{ij}') \tag{9.25}$$

where

$$\begin{aligned} \lambda &= \lambda(\Delta, \mathcal{S}, x_i) \\ \eta &= \eta(\Delta, \mathcal{S}, x_i) \end{aligned} \tag{9.26}$$

are two viscosity coefficients, and

$$e' = \delta_{ij} e_{ij}'. \tag{9.27}$$

In the absence of shear, putting $e_{ij}' = \frac{1}{3} e' \delta_{ij}$, we find

$$T\dot{s}_v^* = \Delta(\lambda + \tfrac{2}{3}\eta) e'^2.$$

The coefficient $\lambda + (\frac{2}{3})\eta$ represents a bulk viscosity for isotropic volume changes. The existence of such a viscosity even for a perfect gas was shown from a statistical viewpoint in a recent paper by Voisin [25]. In most cases this viscosity is neglected by putting

$$\lambda + \tfrac{2}{3}\eta = 0. \tag{9.28}$$

We write the invariants in the form

$$\begin{aligned} e'^2 &= e_{ij}' e_{\mu\nu}' \; \delta_{ij} \; \delta_{\mu\nu} , \\ 2 e_{ij}' e_{ij}' &= e_{ij}' e_{\mu\nu}' (\delta_{i\mu} \; \delta_{j\nu} + \delta_{j\mu} \; \delta_{i\nu}). \end{aligned} \tag{9.29}$$

Hence

$$2\mathfrak{D}_v = \Delta \mathcal{E}_{\mu\nu}{}^{ij} e_{ij}' e_{\mu\nu}' \tag{9.30}$$

where

$$\mathcal{E}_{\mu\nu}{}^{ij} = \mathcal{E}_{\nu\mu}{}^{ij} = \mathcal{E}_{\mu\nu}{}^{ji} = \mathcal{E}_{ij}{}^{\mu\nu} = \lambda \delta_{ij} \delta_{\mu\nu} + \eta(\delta_{i\mu}\delta_{j\nu} + \delta_{j\mu}\delta_{i\nu}) \tag{9.31}$$

represents an isotropic viscosity tensor. We substitute the values (9.11) of e_{ij}' into expression (9.31). This yields

$$2\mathfrak{D}_v = \Delta B_{jk} B_{\nu l} \mathcal{E}_{\mu l}{}^{ik} \dot{a}_{ij} \dot{a}_{\mu\nu} . \tag{9.32}$$

The rate of dissipation in the unit element due to thermal conduction is obtained from (8.5) and (9.20):

$$2\mathfrak{D}_T = T\dot{s}_T^* = T\lambda_{ij} \dot{S}_i \dot{S}_j . \tag{9.33}$$

The total rate of entropy production in the unit element is

$$\dot{s}^* = \dot{s}_v^* + \dot{s}_T^* = \frac{2}{T}(\mathfrak{D}_v + \mathfrak{D}_T) \tag{9.34}$$

and the corresponding virtual dissipation is

$$T \; \delta s^* = \frac{\partial \mathfrak{D}_v}{\partial \dot{a}_{ij}} \, \delta a_{ij} + \frac{\partial \mathfrak{D}_T}{\partial \dot{S}_i} \, \delta S_i . \tag{9.35}$$

The principle of virtual dissipation (2.20) for the whole fluid is written

$$\int_\Omega (\delta_R \mathcal{V} + \rho \ddot{u}_i \; \delta u_i - \rho \mathcal{B}_i \; \delta u_i + T \; \delta s^*) \, d\Omega \tag{9.36}$$

where

$$\delta_R \mathcal{V}(\Delta, s + s^*, x_i) = \frac{\partial \mathcal{V}}{\partial \Delta} \frac{\partial \Delta}{\partial a_{ij}} \, \delta a_{ij} + \frac{\partial \mathcal{V}}{\partial s} \, \delta s \tag{9.37}$$

and

$$a_{ij} = \partial u_i / \partial x_j , \qquad s = -\partial S_i / \partial x_i . \tag{9.38}$$

We substitute the values (9.35) and (9.37) of $T\delta s^*$ and $\delta_R\mathcal{V}$ into the integral (9.36) and integrate by parts using the holonomic constraints (9.38). We vary δu_i and δS_i arbitrarily inside Ω. This yields

$$\begin{gathered}\frac{\partial}{\partial x_j}\left(\frac{\partial\mathcal{V}}{\partial\Delta}\frac{\partial\Delta}{\partial a_{ij}} + \frac{\partial\mathfrak{D}_v}{\partial\dot{a}_{ij}}\right) + \rho\mathcal{B}_i = \rho\ddot{u}_i\ ,\\ \frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{V}}{\partial s}\right) + T\lambda_{ij}\dot{S}_j = 0.\end{gathered} \tag{9.39}$$

Thus we obtain six field equations which govern the motion and heat conduction of a compressible heterogeneous Newtonian fluid. We remember that ρ represents the initial density at x_i and $\mathcal{B}_i$ is the body force at $x_i + u_i$. In addition to u_i and s_i , there is a seventh variable involved, s^*, which is the entropy produced by the friction and by heat conduction. The additional equation is (9.34).

In the particular case of an incompressible isothermal homogeneous Newtonian fluid a virtual work principle was formulated by Lieber [26].

Non-Newtonian fluid. It is easy to show that the relation between the instantaneous stress σ_{ij}' due to strain rate e_{ij}' for a nonlinear fluid (see Appendix) has the form

$$\sigma_{ij}' = F_1\delta_{ij} + F_2 e_{ij}' + F_3 e_{ik}' e_{kj}' \tag{9.40}$$

where F_1 , F_2 , F_3 are functions of the three strain rate invariants

$$\begin{aligned} I_1 &= e' = e_{ij}'\ \delta_{ij}\ ,\\ I_2 &= e_{ij}' e_{ij}',\\ I_3 &= e_{ij}' e_{jk}' e_{ki}'. \end{aligned} \tag{9.41}$$

as well as the change of volume Δ, the local entropy $\mathcal{S}$ and the initial corrdinates x_i if the fluid in non-homogeneous. We write

$$F_i = F_i(I_1\ , I_2\ , I_3\ , \Delta, \mathcal{S}, x_k). \tag{9.42}$$

The rate of dissipation of the unit element is

$$T\dot{s}_v{}^* = \Delta\sigma_{ij}' e_{ij}'.$$

We note that, using expression (9.11) for e_{ij}', the viscous stress written as a function of a_{ij} , $\dot{a}_{ij}$, Δ, $\mathcal{S}$ and x_i is

$$\sigma_{ij}' = \sigma_{ij}'(a_{\mu\nu}\ , \dot{a}_{\mu\nu}\ , \Delta, \mathcal{S}, x_k). \tag{9.43}$$

From expression (2.22), considering frozen dissipative forces σ_{ij}', the virtual dissipation due to viscosity is

$$T\delta s_v{}^* = \tfrac{1}{2}\ \Delta\sigma_{ij}'\left(\frac{\partial\,\delta u_i}{\partial\xi_j} + \frac{\partial\,\delta u_j}{\partial\xi_i}\right). \tag{9.44}$$

Since time differentials and variations play the same role we may use (9.11) and obtain

$$\frac{1}{2}\left(\frac{\partial}{\partial\xi_j}\ \delta u_i + \frac{\partial}{\partial\xi_i}\ \delta u_j\right) = \tfrac{1}{2}(B_{kj}\ \delta a_{ik} + B_{ki}\ \delta a_{jk}). \tag{9.45}$$

Hence the virtual dissipation due to viscosity is

$$T\delta s_v{}^* = R_{ij}\delta a_{ij} \tag{9.46}$$

with

$$R_{ij} = \Delta\sigma_{ik}'B_{jk} . \tag{9.47}$$

We substitute this expression of $T\delta s_v{}^*$ in the principle of virtual dissipation (2.20) and proceed as in the case of the Newtonian fluid. We obtain the field equations

$$\frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{V}}{\partial \Delta}\frac{\partial \Delta}{\partial a_{ij}} + R_{ij}\right) + \rho\mathcal{B}_i = \rho\ddot{u}_i , \qquad \frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{V}}{\partial s}\right) + T\lambda_{ij}\dot{S}_j = 0, \tag{9.48}$$

The seventh equation for the rate of entropy production is now

$$\dot{s}^* = \frac{2\mathfrak{D}_T}{T} + \frac{\Delta}{T}\sigma_{ij}'e_{ij}' . \tag{9.49}$$

Lagrangian equations for Newtonian and non-Newtonian fluids. Using the quasi-holonomic approximation

$$\mathcal{S} = s,$$

i.e. assuming that the entropy production does not contribute significantly to the thermodynamic state of the system, we may derive general Lagrangian equations for linear and non-linear compressible viscous fluids with heat conduction. Isothermal and quasi-isothermal cases are also holonomic.

The fluid is now completely described by two fields expressed by Eqs. (5.23), i.e.

$$\begin{aligned} u_i &= u_i(q_1 , q_2 \cdots q_n , x_l , t), \\ S_i &= S_i(q_1 , q_2 \cdots q_n , x_l , t). \end{aligned} \tag{9.50}$$

They represent material and entropy displacements as functions of generalized coordinates q_i . The collective potential (9.14) is now

$$V = \int_\Omega \mathcal{V}(\Delta, s, x_i)\, d\Omega = V(q_1 , q_2 \cdots q_n , t). \tag{9.51}$$

For a Newtonian fluid the dissipation function is

$$D = \int_\Omega (\mathfrak{D}_v + \mathfrak{D}_T)\, d\Omega \tag{9.52}$$

where $\mathfrak{D}_v$ and $\mathfrak{D}_T$ are defined by (9.32) and (9.33).

It embodies the total dissipation due to viscous friction and heat conduction. If the body force is derived from a potential G such as gravity we introduce a mixed collective potential $\mathcal{P}$ as given by (5.31). We may write

$$\mathcal{P}(q_1 , q_2 \cdots q_n , t) = V + G \tag{9.53}$$

Lagrangian equations for the Newtonian fluid may then be derived as Eqs. (8.24) for thermoelasticity. They are

$$\frac{d}{dt}\left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{T}}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \tag{9.54}$$

The kinetic energy $\mathcal{T}$ is defined by expression (5.34) and Q_i is a thermomechanical boundary force which is given by Eq. (5.33) and takes into account both mechanical and thermal boundary forces.

If the fields (9.50) do not contain the time explicitly, the kinetic energy (5.34) and the dissipation function (9.52) are quadratic forms in $\dot{q}_i$ as in Eqs. (8.21), (8.22).

For a non-Newtonian fluid the Lagrangian equations are the same as (9.54) except for the dissipative term. The virtual dissipation of the whole fluid due to viscosity is derived by integrating the dissipation of the unit element (9.46) over the volume Ω. We write

$$\int_\Omega T\,\delta s_v{}^* = \int_\Omega R_{ij}\,\delta a_{ij}\,d\Omega = R_i\,\delta q_i \tag{9.55}$$

where

$$R_i = \int_\Omega R_{kj}\,\frac{\partial a_{kj}}{\partial q_i}\,d\Omega. \tag{9.56}$$

The Lagrangian equations for the non-Newtonian fluid are

$$\frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathfrak{T}}{\partial q_i} + \frac{\partial D_T}{\partial \dot{q}_i} + R_i + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \tag{9.57}$$

where

$$D_T = \int_\Omega \mathfrak{D}_T\,d\Omega \tag{9.58}$$

is the dissipation function due to heat conduction.

10. Linear viscodynamics. Of special interest is the Lagrangian formulation of incompressible viscous Newtonian fluids for small motions and negligible thermal effects. Following a terminology used earlier by the author in the analysis of acoustic propagation [5], such a system may be called *viscodynamic*. Linear viscodynamics involves essentially the interaction of viscous and dynamic forces in analogy with linear viscoelasticity which envolves the interaction of linear dissipative or viscous forces with elastic forces.

The small displacement field of the fluid is represented by

$$u_i = u_{ij}q_j \tag{10.1}$$

where $u_{ij}(x_l)$ are given fields, satisfying incompressibility, and q_i are generalized coordinates. The kinetic energy and the dissipation function are

$$\mathfrak{T} = \tfrac{1}{2}m_{ij}\dot{q}_i\dot{q}_j\,, \qquad D = \tfrac{1}{2}b_{ij}\dot{q}_i\dot{q}_j\,. \tag{10.2}$$

The Lagrangian equations are

$$m_{ij}\ddot{q}_j + b_{ij}\dot{q}_j = Q_i \tag{10.3}$$

where Q_i are the generalized forces applied at the boundary. Body forces are neglected. Operationally we put $p = d/dt$ and write

$$(m_{ij}p + b_{ij})pq_j = Q_i\,. \tag{10.4}$$

Except for the replacement of q_i by pq_i, Eqs. (10.4) are mathematically the same as those of linear viscoelasticity. If there is a large number of internal coordinates, i.e. internal velocity fields such that $Q_i = 0$, relations between observed velocities and applied forces are related by

$$\dot{q}_i = \hat{A}_{ij} Q_j , \qquad Q_i = \hat{Z}_{ij} \dot{q}_j \tag{10.5}$$

where $\hat{A}_{ij}$ and $\hat{Z}_{ij}$ are the symmetric operators (6.4). For example at high frequency, i.e. for $p = i\omega$ (with a large value of the circular frequency ω), we write

$$Q_i = Z_{ij}' p^2 q_j . \tag{10.6}$$

This relation is purely inertial and the system behaves as a perfect fluid.

Acoustic propagation in porous solids. We have applied the previous results in a theory of acoustic propagation in a porous solid by generalizing Darcy's law in the form [5, 6]

$$-\frac{\partial p}{\partial x_i} = \hat{Y}_{ij} \dot{w}_j , \tag{10.7}$$

where $\partial p / \partial x_i$ is the pressure gradient of the pore fluid and $\dot{w}_i$ is the volumetric velocity of the pore fluid relative to the solid. The viscodynamic operator is

$$\hat{Y}_{ij} = \sum^{s} \frac{p}{r_s + p} Y_{ij}^{(s)} + Y_{ij} + Y_{ij}' p \tag{10.8}$$

where $\hat{Y}_{ij}$ is a symmetric operational tensor of second order. It is interesting to note that if the pore geometry exhibits cubic symmetry, as in the case of piled spheres, the tensor $\hat{Y}_{ij}$ is isotropic. For high frequencies the viscodynamic operator reduces to $Y_{ij}' p$ which represents purely inertial effects of a perfect fluid, while at low frequency it becomes Y_{ij} corresponding to Poiseuille flow and the classical Darcy's law. The variation of $\hat{Y}_{ij}$ with frequency is due to the change in microvelocity fields in the pores from Poiseuille flow to potential flow. It may be looked upon as due to the change of amplitude of the various microvelocity fields $u_{ij} \dot{q}_j$ which play the role of internal coordinates.

11. Thermodynamics of instability. Basically there are two fundamentally different types of instabilities which may be considered. One type is an unstable static equilibrium, the other is the instability in the vicinity of a steady state [34].

Unstable static equilibrium. The linearized Lagrangian equations for perturbations q_i in the vicinity of an equilibrium state are

$$\frac{d}{dt}\left(\frac{\partial \mathfrak{T}}{\partial \dot{q}_i}\right) + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = 0 \tag{11.1}$$

where $\mathfrak{T}$, $\mathfrak{D}$, $\mathcal{P}$ are the quadratic forms (6.1) for the kinetric energy the dissipation functions and the mixed collective potential. Equilibrium corresponds to $\mathcal{P} = 0$. It may be unstable if $\mathcal{P}$ is not positive definite. It was shown [7, 14] that instability of this type is *non-oscillatory*. A typical example is thermoelastic buckling discussed extensively earlier [10, 14]. It was pointed out that incipient isothermal buckling [10] occurs for a buckling load derived from isothermal elastic moduli. Creep buckling occurs at a rate controlled by the thermal conductivity of the purely elastic material.

As shown in [14], it provides a mechanical model for the more general case of an unstable thermodynamic equilibrium at *minimum entropy*.

The case of buckling of an embedded viscoelastic layer in a viscoelastic medium was also analyzed, showing that the physical behavior is *fundamentally conditioned by the thermodynamics* [13].

Dissipative structures for unstable linear systems. A horizontally stratified system of incompressible Newtonian fluids in a gravity field with density inversions, i.e. when some layers are denser than those below, provides an example of a linear dissipative system for small motion. The system is in unstable static equilibrium when the layers are horizontal. The case has been extensively analyzed in the context of geophysics [7, 27, 28]. A fundamental aspect of the physics may be illustrated on the simple case [7] of a viscous layer of viscosity η, thickness h, and density ρ lying on a rigid base, surmounted by a semi-infinite medium of viscosity η' and density ρ'. It was shown [7] that the effect of the gravity field is the same as applying a vertical force f per unit area at the interface equal to

$$f = (\rho' - \rho)gw(x) \tag{11.2}$$

where g is the gravity acceleration and w is the vertical deflection of the interface along the horizontal direction x. Assume a sinusoidal deflection of the interface

$$w = q \cos lx. \tag{11.3}$$

Consider a vertical slab of unit thickness of the system. Per unit length along x the change in potential due to gravity is obviously (L large)

$$\mathcal{P} = -\frac{1}{2L}\int_0^L fw\,dx = -\tfrac{1}{4}(\rho' - \rho)gq^2. \tag{11.4}$$

Similarly, the dissipation function must be of the form

$$D = \tfrac{1}{2}b\dot{q}^2 \tag{11.5}$$

where b depends on the wavelength. The Lagrangian equation is

$$\frac{\partial \mathcal{P}}{\partial q} + \frac{\partial D}{\partial \dot{q}} = 0. \tag{11.6}$$

For a solution

$$q \approx \exp(pt), \tag{11.7}$$

Eq. (11.6) leads to

$$p = \tfrac{1}{2}\frac{(\rho' - \rho)}{b}g. \tag{11.8}$$

The wavelength for which b is minimum yields the maximum value of p and the fastest rate of growth of the deflection. The corresponding wavelength was called the *dominant wavelength*, and represents a *dissipative structure* which will gradually emerge for any initial perturbation of the interface.

The existence of dissipative structures away from equilibrium was postulated by Prigogine and Glansdorff [29] as due to nonlinearity. The foregoing discussion shows that such dissipative structures are also generated in unstable linear systems in the vicinity of equilibrium [34].

Note that a fluid layer heated from the bottom is not in initial thermodynamic equilibrium but in an initial state of thermal flow. Hence oscillatory instability is not excluded in this case [33].

Instability in the vicinity of a steady state. The concept of steady state may be defined as one where the generalized coordinates are either linear or almost linear functions of time for time intervals within certain limits. We represent the steady state as

$$q_i = \varphi_i(t) \tag{11.9}$$

where φ_i are linear or almost linear. Assuming a holonomic system, the stability may be analyzed by a perturbation methods, writing the generalized coordinates as

$$q_i = \varphi_i(t) + q_i' \tag{11.10}$$

where q_i' are unknown small perturbations.

While the procedure is quite general, we may simplify the analysis by restricting ourselves to a formulation in terms of intrinsic dissipative forces and to systems where inertia forces are negligible. The Lagrangian equations (2.30) for such systems are

$$\frac{\partial \mathcal{P}}{\partial q_i} + R_i = Q_i\,. \tag{11.11}$$

We denote by $\overline{\partial \mathcal{P}}/\partial q_i$ and $\bar{R}_i$ the values $\partial \mathcal{P}/\partial q_i$ and R_i for the steady state solution $\varphi_i(t) = q_i$. Since the steady state is a solution of the Lagrangian equations (11.11) of the system, we may write

$$\frac{\overline{\partial \mathcal{P}}}{\partial q_i} + \bar{R}_i = Q_i\,. \tag{11.12}$$

Perturbed values are

$$\begin{aligned} \frac{\partial \mathcal{P}}{\partial q_i} &= \frac{\partial \mathcal{P}}{\partial q_i} + \frac{\partial^2 \mathcal{P}}{\partial q_i\,\partial q_j}\,q_j', \\ R_i &= \bar{R}_i + \frac{\partial \bar{R}_i}{\partial q_j}\,q_j' + \frac{\partial \bar{R}_i}{\partial \dot{q}_j}\,\dot{q}_j', \end{aligned} \tag{11.13}$$

where $\partial^2\overline{\mathcal{P}}/\partial q_i\partial q_j$, $\partial \bar{R}/\partial q_i$ and $\partial \bar{R}/\mathcal{P}\dot{q}_i$ are the unperturbed values of $\partial^2\mathcal{P}/\partial q_i\partial q_j$, $\partial R/\partial q_i$, and $\partial R/\partial \dot{q}_i$. Substitution of the perturbed values (11.13) in the Lagrangian equations (11.11), taking into account Eqs. (11.12), yields

$$\mathcal{A}_{ij} q_j' + \mathcal{B}_{ij} \dot{q}_j' = 0 \tag{11.14}$$

with

$$\mathcal{A}_{ij} = \frac{\partial^2 \mathcal{P}}{\partial q_i\,\partial q_j} + \frac{\partial \bar{R}_i}{\partial q_j}\,; \qquad \mathcal{B}_{ij} = \frac{\partial \bar{R}_i}{\partial \dot{q}_j}\,. \tag{11.15}$$

Eqs. (11.14) for the perturbations q_i' may have increasing or decreasing solutions indicating stability of instability of the steady state. However, the assumption of symmetry of $\mathcal{A}_{ij}$ and $\mathcal{B}_{ij}$ and positive-definiteness of $\mathcal{B}_{ij}$ is not valid in this case, hence unstable solutions *may be oscillatory.*

It is interesting to examine the case of a quasi-reversible system with a dissipation function D and a corresponding dissipative force R_i :

$$D = \tfrac{1}{2} b_{ij}(q_k)\dot{q}_i\dot{q}_j \, , \qquad R_i = \frac{\partial D}{\partial \dot{q}_i} = b_{ij}(q_k)\dot{q}_j \, . \tag{11.16}$$

In this case

$$\mathcal{A}_{ij} = \frac{\partial^2 \mathcal{P}}{\partial q_i \, \partial q_j} + \frac{\partial \bar{b}_{ik}}{\partial q_j} \dot{\varphi}_k \, , \qquad \mathcal{B}_{ij} = \bar{b}_{ij} \tag{11.17}$$

where $\bar{b}_{ij}$ and $\partial \bar{b}_{ik}/\partial q_j$ are the values of b_{ij} and $\partial b_{ik}/\partial q_j$ for $q_i = \varphi_i(t)$. Note that in this case $\mathcal{B}_{ij}$ is symmetric and positive-definite. However, there may be cases where $(\partial \bar{b}_{ik}/\partial q_j)\dot{\varphi}_k \cong (\partial \bar{b}_{jk}/\partial q_i)\dot{\varphi}_k$. In such cases we also have $\mathcal{A}_{ij} \cong \mathcal{A}_{ji}$ and the instability is *non-oscillatory*. An example of such a case is given below.

Dissipative structure for an unstable steady state. Folding instability of a stratified viscous medium in compression. As an example of instability in the vicinity of a steady state leading to a dissipative structure, consider a highly viscous layer embedded in an infinite medium of much smaller viscosity. The materials are assumed incompressible and we neglect body forces and temperature changes; hence we put $\mathcal{P} = 0$.

Consider an initial length L of the layer, along the middle plane which coincides with the x axis. We assume that the whole system is compressed in the direction of the layer at a constant rate, so that the initial distance L at $t = 0$ becomes

$$L' = L - \beta t \tag{11.18}$$

at time t. We may take

$$\varphi_0(t) = \beta t \tag{11.19}$$

to be the generalized coordinate describing the initial steady state. The perturbation is the lateral deflection $w(x, t)$ of the layer normal to its initial plane. It may be written as a Fourier expansion

$$w = \sum^{n} q_n' \sin l_n x \tag{11.20}$$

where $l_n = \pi n/L$ $(n = 1, 2, \cdots)$ and q_n' are the perturbations of the initial steady state.

We first evaluate the dissipation function of the layer. The deformation is assumed to be an incompressible plane strain with principal strains ϵ_1 and ϵ_2 satisfying the condition of incompressibility $\epsilon_1 + \epsilon_2 = 0$. Applying expression (9.25) to this case, the dissipation function of the layer per unit transversal dimension normally to the plane strain is

$$D_l = 2\eta_1 \int_0^L dx \int_{-h/2}^{+h/2} \dot{\epsilon}_1^{\,2} \, dy \tag{11.21}$$

where y is measured along the thickness h of the layer of viscosity η_1. The strain is

$$\epsilon_1 = \frac{1}{2L} \int_0^L \left(\frac{\partial w}{\partial x}\right)^2 dx - y \frac{\partial^2 w}{\partial x^2} - \frac{\beta t}{L} \, . \tag{11.22}$$

The second term represents the bending strain. Substituting (11.20) and (11.22) in (11.21) and neglecting higher-order terms in q_n', we obtain

$$D_l = \frac{1}{12} L \eta_1 h^3 \sum^{n} l_n^{\,4} \dot{q}_n'^{\,2} - 2\eta_1 \beta h \sum^{r} l_n^{\,2} q_n' \dot{q}_n' + 2\eta_1 \frac{\beta^2 h}{L} \tag{11.23}$$

The dissipation function of the two half-spaces on each side of the layer is easily obtained by distributing a sinusoidal load

$$F_n(x) = F_n \sin l_n x \tag{11.24}$$

on the half-space, producing a rate of deflection of the surface

$$\dot{w}_n(x) = \dot{q}_n' \sin l_n x. \tag{11.25}$$

The relation between F_n and $\dot{q}_n$ has been evaluated many times earlier [7, 13]. We find

$$F_n = 2 l_n \eta_2 \dot{q}_n' \tag{11.26}$$

where η_2 is the viscosity of the half-space. The dissipation function of the two half-spaces is expressed in terms of the total power dissipated as

$$D_m = \int_0^L \sum^n F_n(x) \dot{w}_n(x)\, dx = L\eta_2 \sum^n l_n \dot{q}_n'^2. \tag{11.27}$$

The total dissipation function is

$$D = D_l + D_m \tag{11.28}$$

and the Lagrangian equations for the perturbations are

$$\partial D / \partial \dot{q}_n' = 0 \tag{11.29}$$

or

$$-2\eta_1 \beta h l_n^2 q_n' + L(\tfrac{1}{6}\eta_1 h^3 l_n^4 + 2\eta_2 l_n)\dot{q}_n' = 0. \tag{11.30}$$

These equations are uncoupled and the solution of each equation is

$$q_n' = C_n e^{p_n t} \tag{11.31}$$

where C_n are constants and

$$p_n = \frac{2\eta_1 \beta}{L}\left[\tfrac{1}{6}\eta_1 h^2 l_n^2 + \frac{2\eta_2}{h l_n}\right]^{-1}. \tag{11.32}$$

This value p_n depends on l_n and hence on the wavelength. If we consider l_n to vary continuously, p_n is maximum for

$$l_n h = (6\eta_2/\eta_1)^{1/3}. \tag{11.33}$$

This corresponds to a wavelength $\mathcal{L} = 2\pi / l_n$ whose amplitude grows at the fastest rate, and which was referred to in earlier work as the *dominant wavelength* [7, 13]. Thus we end up with an unstable phenomenon showing a regular sinusoidal pattern which emerges gradually as a dissipative structure. Note that in this particular case the instability is *non-oscillatory* although the initial state is not one of thermodynamic equilibrium.

The case of a single layer considered above is a particular case of a very general phenomenon of viscous buckling of a stratified viscous medium in compression. Its general theory has been treated extensively earlier [7]. It illustrates the properties of a thermodynamic system in an unstable steady flow generating a dissipative structure in the form of regular folds. This phenomenon is fundamental in the theory of geological structures of sedimentary rock, as well as the theory of creep buckling of composite multilayered plates.

It should be noted that Eq. (11.29) expresses *minimum dissipation* where $\dot{q}_i'$ are varied arbitrarily. This is a particular case of the general theorem of Sec. 3.

Dominant unstable structures. Minimum principle. As shown by the previous examples, unstable perturbations in many cases may be governed by equations of the type

$$\mathcal{A}_{ij} q_j' + \frac{\partial \bar{D}}{\partial \dot{q}_i'} = 0 \tag{11.34}$$

where

$$\bar{D} = \tfrac{1}{2} \bar{b}_{ij} \dot{q}_i' \dot{q}_j' \tag{11.35}$$

with constant coefficients $\mathcal{A}_{ij}$ and $\bar{b}_{ij}$. For a system initially in unstable static equilibrium, a general theorem [7, 14] shows that the instability is *non-oscillatory.* This is a consequence of the symmetry property $\mathcal{A}_{ij} = \mathcal{A}_{ji}$ and the positive-definite character of the dissipation function $\bar{D}$. For the case of instability in the vicinity of a steady state this may not be applicable. However, in the particular example (11.30) for an initial steady state the symmetry property ($\mathcal{A}_{ij} = \mathcal{A}_{ji}$) is valid and as a consequence the instability is non-oscillatory. In all such cases we may of course apply the minimum instantaneous dissipation theorem of Eqs. (3.6) and (3.7). However, we may formulate an additional minimum property by considering the exponential characteristic modal solutions

$$q_i'^{(s)} = C_s e^{p_s t} \tag{11.36}$$

for those cases where the characteristic values p_s are real and positive. The particular modal solution for which p_s is maximum represents a dominant structure which will emerge after sufficient time. This structure is *independent of the initial conditions.* In the two examples discussed above, one of unstable equilibrium of a layered fluid under gravity, and the other of folding instability and a layered viscous medium initially undergoing a steady compressive flow, the dominant structure is a periodic sinusoidal spatial distribution. For each modal solution we may write

$$p_s = -\frac{\mathcal{A}_{ij} q_i'^{(s)} q_j'^{(s)}}{\bar{b}_{ij} q_i'^{(s)} q_j'^{(s)}}. \tag{11.37}$$

The dominant structure is such that

$$\bar{b}_{ij} q_i'^{(s)} q_j'^{(s)} = \text{minimum} \tag{11.38}$$

for

$$\mathcal{A}_{ij} a_i'^{(s)} q_j'^{(s)} = \text{constant}. \tag{11.39}$$

Appendix. Stress-strain law for non-Newtonian fluids. The most general relation between stress and strain-rate for a non-Newtonian isotropic fluid may be derived quite simply as follows. Because of isotropy, principal directions of stress coincide with principal directions of strain-rate. We may write the principal stresses $\sigma_1'\sigma_2'\sigma_3'$ as functions of the principal strain-rates $e_1'e_2'e_3'$ in the form

$$\begin{aligned} \sigma_1 &= F_1 + F_2 e_1' + F_3 e_1'^2, \\ \sigma_2 &= F_1 + F_2 e_2' + F_3 e_2'^2, \\ \sigma_3 &= F_1 + F_2 e_3' + F_3 e_3'^2, \end{aligned} \tag{A.1}$$

where F_1, F_2, F_3 are three functions of e_1', e_2', e_3'. It is always possible to write the stresses in this form since we may consider Eqs. (A.1) to determine F_1, F_2, F_3 as three unknowns. The system of equations, and hence the unknowns, remain the same for all permutations of the indices for σ_i and e_i'. Therefore $F_1F_2F_3$ are symmetric functions of $e_1'e_2'e_3'$ and hence functions only of the invariants

$$I_1 = e_{ij}'\delta_{ij}, \qquad I_2 = e_{ij}'e_{ij}', \qquad I_3 = e_{ij}'e_{jk}'e_{ki}', \tag{A.2}$$

$$\begin{aligned} F_1 &= F_1(I_1, I_2, I_3) \\ F_2 &= F_2(I_1, I_2, I_3) \\ F_3 &= F_3(I_1, I_2, I_3) \end{aligned} \tag{A.3}$$

Finally, for directions other that the principal directions we may write (A.1) as

$$\sigma_{ij}' = F_1\delta_{ij} + F_2e_{ij}' + F_3e_{ik}'e_{kj}' \tag{A.4}$$

which establishes relations (9.40). For an incompressible fluid this yields the result of Reiner [30] and Rivlin [31]. The particular case $\sigma_{ij}' = \partial D/\partial e_{ij}'$ where D is a function of the invariants was discussed by Ziegler [32].

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