LINEAR THERMODYNAMICS AND THE MECHANICS OF SOLIDS

The Thermodynamics of linear irreversible processes is presented from a unified viewpoint. This provides a new and synthetic approach to the linear mechanics of deformation of solids, which includes as particular cases the classical theory of Elasticity. Thermoelasticity and Viscoelasticity. The first two sections constitute an introduction to the general concepts and principles of linear Thermodynamics as developed in the writer's earlier work and presented in somewhat more detail. This is followed by the application of the general thermodynamic theory to Thermoelasticity which combines the theories of Elasticity, Heat Transfer, and their coupled effects into a single treatment. Some immediate consequences are derived such as the property of diffusion of entropy and certain fundamental relations with reference to thermal stresses. The introduction of inertia forces leads to a general formulation of thermoelastic dissipation of dynamical systems by Lagrangian methods. The second order heat produced by the dissipation is evaluated. Linear Viscoelasticity and Relaxation Phenomena are also a particular case of the thermodynamic theory. The resulting stress-strain relations with heredity properties are discussed. The operational formulation of these relations leads naturally to a formal correspondence with the theory of Elasticity and to an operational-variational principle. The latter provides a generalization of Lagrange's equations in integro-differential form to the dynamics and stress analysis of viscoelastic structures. Some specific applications of these principles are presented.

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Introduction

In recent years new and remarkably fruitful concepts and methods have been introduced in Thermodynamics which lead to a phenomenological approach for irreversible phenomena. The major contribution was made by Onsager in 1931 when he introduced his now famous reciprocity relations. In the realm of linear phenomena the treatment of thermodynamics can be made completely systematic and general. Application of this general thermodynamics is of considerable interest in the field of linear mechanics of solids. In the course of a general research program on the mechanical properties of rock we developed a general formulation of irreversible phenomena which uses generalized coordinates and Lagrangian concepts and is applicable to a very wide class of phenomena. The theory was subsequently applied to Viscoelasticity. Thermoelasticity and Heat Transfer and the mechanics of porous media bringing these phenomena within the scope of a single more general theory. It also provides a new foundation for the classical theory of Elasticity.

We have attempted to present a perspective of this development. Some new results are also included. We have dwelt in somewhat more detail than in the original papers on the derivation of the basic thermodynamic equations, which is the object of Sections 2 and 3. The concept of hidden coordinates and the "black box" approach to a thermodynamic system lead directly to relaxation and heredity laws. The resulting expression for the impedance matrix is readily applied to the stress-strain relations of viscoelasticity as presented later in Section 6. The symbolism of the operational calculus has been preferred since it is most convenient in applications.

The field of Thermoelasticity which is understood here to include thermal stresses, thermoelastic damping and heat transfer is treated in Sections 4 and 5. It constitutes an excellent subject for illustrating the new principles.

A general formulation of linear viscoelasticity, i.e. the mechanics of materials which exhibit relaxation and heredity effects, follows immediately from the general thermodynamic theory, particularly from the expression developed for the thermodynamic impedance. This is discussed in Section 6 and special emphasis is put on the specific features of the operators which depend on thermodynamics. We conclude in Section 7 with applications to the stress analysis and dynamics of viscoelastic structures and review some general properties which are direct consequences of a correspondence rule and an operational-variational principle.

Generalized Concepts of Free Energy and Dissipation Function

We shall first introduce the conceptual and mathematical foundation of the linear thermodynamics of irreversible processes and elaborate somewhat beyond the original presentation as developed in several earlier papers [1], [2], [3].

Throughout the text we shall use the word thermodynamics as referring to irreversible processes and reserve the term thermostatics for the description of equilibrium states.

Let us consider a thermodynamic system designated as system I and whose thermodynamic state is defined by a number of state variables, q_i .

We now introduce a heat reservoir as system II. It is assumed that systems I and II can exchange heat but that system II is large enough so that its temperature T_r remains constant, (Fig. 1).

The total system I + II is then considered as an isolated system, and the state variables q_i are chosen in such a way that $q_i = 0$ corresponds to thermostatic equilibrium. For this equilibrium condition the systems I and II is at a uniform temperature T_r which may then be called the *reference temperature*. Values of q_i different from zero measure the departure of the system from its equilibrium state.

In general it will be assumed that the departure from equilibrium is small and that the system is linear in the sense that the principle of super-position applies. The variables q_i considered here are of an extremely general nature; they may be scalars, such as distributed temperatures, pressure concentration of chemical species or vector fields such as geometric displacements, mass and heat displacements, etc.

In the following we shall talk about the entropy of a thermodynamic system which is not in equilibrium. This is, of course, justified if we use the Boltzman definition of entropy based on statistical mechanics. On the other hand, the classical thermodynamic definition while applying strictly only to a system in equilibrium may be extended as an approximation to systems in the vicinity of equilibrium. This has been further justified by Prigogine [4]¹ on the basis of gas-kinetic theory. In this definition it is assumed that local temperature and entropy may be defined on the basis of thermostatic definitions and the total entropy is the total sum of the local values. It has been found that these concepts apply to a very wide class of phenomena some of which are not necessarily restricted to small departures from equilibrium. In addition the thermostatic concepts may even be used separately to describe internal degrees of freedom which are on the same geometrical location but are not in mutual equilibrium such as the molecular or electronic degrees of freedom of a gas.



FIGURE 1. PRIMARY SYSTEM AND HEAT RESERVOIR.

The next step is to consider the system I + II as disturbed from equilibrium. The departure from equilibrium is defined by the values of the state variables q_i and for each configuration of the system away from equilibrium there is a velocity vector whose components q_i in the configuration space are the time derivatives of q_i . These components are also called "fluxes." From the classical principles of thermostatics we know that the entropy of an isolated system in *stable* equilibrium is a maximum. Hence the entropy S' of the isolated system I + II is a maximum which may be arbitrarily chosen as zero. Limiting the expansion to the quadratic terms we may therefore write

$$-TS' = \frac{1}{2}a_{ij}q_iq_j$$
 (2.1)

which is a non-negative quadratic form.

We have written the expansion for $-T_rS'$ rather than S' because, as will be seen below $-T_rS'$ turns out to be the generalization of the concept of potential energy in classical mechanics. The derivatives $T_r\partial S'/\partial q_i$ are a measure of the departure of the system from equilibrium and play the role of "restoring forces." The assumption of linearity leads to linear relations between the rate variables \dot{q}_i and q_i . They may be written

$$T_r \frac{\partial S'}{\partial q_i} = b_{ij} \dot{q}_j \qquad (2.2)$$

At this point the reprocity relations established by Onsager [5] [6] may be introduced. In the present formulation they are equivalent to the statement that the matrix of b_{ij} 's is symmetric,

$$b_{ij} = b_{ji} \tag{2.3}$$

This important property leads immediately to the existence of a quadratic form

$$D = \frac{1}{2} b_{ij} \dot{q}_i \dot{q}_j \qquad (2.4)$$

such that (2.2) may now be written

$$T_r \frac{\partial S'}{\partial q_i} = \frac{\partial D}{\partial \dot{q}_i}$$
(2.5)

¹See also, for instance, [12] page 221.

As pointed out above the function $-T_rS'$ plays the same role as the potential energy in the more restricted field of mechanics. We put

$$V = -T_r S' = \frac{1}{2} a_{ij} q_i q_j$$
(2.6)

and (2.5) become

$$\frac{\partial V}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} = 0 \qquad (2.7)$$

What is the significance of the function D? Multiplying (2.5) by \dot{q}_i and adding we derive,

$$T_r \frac{\partial S}{\partial t} = \frac{\partial D}{\partial \dot{q}_i} \dot{q}_i = 2D$$
 (2.8)

In the process of returning to equilibrium the entropy S'of the isolated system cannot decrease, therefore $\partial S'/\partial t \ge 0$ and D is a non-negative quadratic function of the velocities \dot{q}_i Equations (2.7) are identical with those of a mechanical system composed of springs and dashpots. The function D is proportional to the rate of dissipation of energy in the dashpots. The term *dissipation* function is borrowed from mechanics to designate the function D in the more general thermodynamic case. Since $\partial S'/\partial t$ is the rate of production of entropy in the system I + II the dissipation function is

$$D = \frac{1}{2}T_r \times (\text{rate of entropy production})$$
 (2.9)

As regards the function V an important aspect of its thermodynamic significance is added if we express the entropy S' of the system I + II in terms of the thermodynamic functions of the system I alone. We may write

$$S' = S + S_R \tag{2.10}$$

where S is the entropy of system I and S_R the entropy of the heat reservoir II. Denoting by h the heat transferred from system I to system II, conservation of energy requires that

$$U = -h \tag{2.11}$$

where U is the internal energy of system I chosen so that U = -h = 0 at equilibrium. The entropy S_R of the reservoir II is also chosen to be zero at equilibrium, hence,

$$S_R = \frac{h}{T_r} = -\frac{U}{T_r}$$
(2.12)

Substituting in (2.10) we find

$$V = -T_r S' = U - T_r S$$
 (2.13)

We recognize here an expression which looks very much like the free energy of classical thermodynamics. There is, however, one difference in the fact that T_r does not refer to the temperature of system I but to the reference temperature of the heat reservoir II. Expression (2.13) is much more general than the classical free energy since the system I may have an arbitrary distribution of nonuniform temperature. Of course if the transformation is isothermal and occurs at the temperature T_r itself, (2.13) coincides with its classical definition. For want of a better term we have referred to V as the generalized free energy.

An alternate expression for V which is of considerable interest in applications was derived in [3]. We denote by

$$V_r = U_r - T_r S_r \tag{2.14}$$

the classical value of the free energy corresponding to a uniform temperature T_r and by V_c the amount by which Vincreases when the initial temperature T_r at any particular point is raised to $T_r + \theta$ i.e. when a non-uniform distribution of temperature increments θ is imposed on the system without changing the other state variables. We may write

$$V = V_r + V_c \tag{2.15}$$

and

$$V_c = U_c - T_r S_c \tag{2.16}$$

or

$$V_{c} = \iiint_{\tau} dr \left[\int_{0}^{\theta} c d\theta - T_{r} \int_{0}^{\theta} \frac{c d\theta}{T_{r} + \theta} \right]$$

$$V_{c} = \iiint_{\tau} d\tau \int_{0}^{\theta} \frac{c \theta}{T_{r} + \theta} d\theta$$
(2.17)

The above expressions refer to the volume integral over the volume r of system I and c is the specific heat per unit volume for all variables constant except the temperature. For small variations θ we may write

$$V_c = \frac{1}{2} \iiint \frac{c\theta^2}{T_r} dr$$
 (2.18)

Hence

$$V = V_r + \frac{1}{2} \iiint \frac{c\theta^2}{T_r} dr \qquad (2.19)$$

The term V_r represents the classical free energy for isothermal transformations at the reference temperature T_r i.e. when T_r represents the temperature of the system itself instead of just that at the heat reservoir. It is the Helmholtz free energy familiar to the physical chemist. The additional term represents the thermodynamics of power engineering i.e. the heat which may be transformed into useful work. It can be seen that it is an integrated expression for the product of the heat $cd\theta$ by the Carnot efficiency $\theta/(T_r + \theta) \cong \theta/T_r$. Our expression (2.13) and (2.19) may, therefore, be considered as a generalization of the Helmholtz free energy to systems at non-uniform temperature.

With reference to Onsager's relations we should point out that theoretically they are valid only for systems which exhibit *microreversibility*. In the presence of magnetic and Coriolis fields of sufficient intensity they are not applicable. Known examples of this are the Hall effect for electrical conductivity and the Rhigi-Leduc effect for thermal conductivity.

We should also bear in mind that the adjunction of the heat reservoir II does not mean that there is necessarily a heat exchange between I and II. This will depend on the thermodynamic *constraints* and adiabatic transformations are therefore not excluded. However, the constraints must respect energy conservation. Further development on the statistical foundations of the Onsager relations were the object of more recent studies by Onsager and Machlup [7], Machlup and Onsager [8], Callen Barasch and Jackson [9] and Greene and Callen [10]. An introduction to the subject will also be found in [11] [12] [13] and [14].

Response of a System to Arbitrary Perturbations

In a system of springs and dashpots differential equations for the motion of the system may be written immediately by adding to the right-hand side of (2.7) definite functions of time which represent the generalized perturbing forces applied to the system. The question is



FIGURE 2. PRIMARY SYSTEM, HEAT RESERVOIR AND PERTUR-BATION OF PRIMARY SYSTEM.

how to establish the validity of this procedure when disturbances of a general thermodynamic nature are applied to the system I + II composed of system I and its adjoined heat reservoir II at the constant temperature T_r .

Let us adjoin to system I a large energy reservoir I_1 , and assume that I_1 is made up of a large spring exerting a *constant* force F on system I through a piston, the displacement of the piston being x. The entropy S' of the total system I + II + I_1 , may be evaluated by writing the equation of energy conservation for the system. If we denote by h the heat acquired by II, conservation of energy requires

$$U = Fx - h \tag{3.1}$$

where U is the internal energy acquired by I. Hence the entropy acquired by II is

$$S_R = \frac{h}{T_r} = \frac{Fx - U}{T_r} \tag{3.2}$$

The entropy increase S' of the total system $I + II + I_{12}$ is

$$S' = S + S_R = S + \frac{F_x - U}{T_r}$$
 (3.3)

where S is the entropy increase of I. We derive

$$T_r S' = -V + F x \tag{3.4}$$

Similarly if instead of adjoining I_1 , we adjoin a heat reservoir I_2 at a temperature $T_r + \theta$ and call h_2 the heat flowing in from I_2 into I, conservation of energy requires

$$U = h_2 - h \tag{3.5}$$

The total increase of entropy of $I + II + I_2$ is then

$$S' = S - \frac{h_2}{T_r + \theta} + \frac{h}{T_r}$$

or

$$S' = S - \frac{U}{T_r} + h_2 \left(\frac{1}{T_r} - \frac{1}{T_r + \theta} \right)$$
 (3.6)

If $\theta \ll T_r$ we may write,

$$T_r S' = -V + \frac{h_2 \theta}{T_r} \tag{3.7}$$

Denoting by

$$S_2 = \frac{h_2}{Tr} \tag{3.8}$$

the entropy inflow from I_2 into I we finally have

$$T_r S' = -V + S_2 \theta \tag{3.9}$$

We see that S_2 and θ play the same role as the *conjugate* coordinates F and x for the applied force. When the two reservoirs I, and I₂ are added simultaneously the total entropy S' of I + II + I₁ + I₂ is given by

$$T_r S' = -V + F x + S_2 \theta \tag{3.10}$$

An alternate definition of the disturbing force is also obtained by considering the expression (3.15) below. This expression is quite general and if we add any number of energy reservoirs disturbing the original system we may write

$$T_r S' = -V + Q_i q_i \tag{3.11}$$

where Q_i is an intensive quantity representing a force and q_i its conjugate extensive coordinate. As a further example the force could be an electromotive force E and the quantity of electricity q flowing through the system is then the conjugate coordinate leading to a term Eq in expressions $Q_i q_i$. In the case of a chemical reaction the mass M of constituent injected from a reservoir into a particular phase or chemical species is the extensive coordinate while the chemical potential μ of this constituent is the conjugate force. The corresponding term in $Q_i q_i$ is μM . The theory is therefore applicable to an "open system."

We may now apply the same reasoning as in the previous section and assume that Onsager's relations apply to the total isolated system $I + II + I_1 + I_2 + ... I_i$. We may then write as above (2.5),

$$T_r \frac{\partial S'}{\partial q_i} = b_{ij} \dot{q}_j = \frac{\partial D}{\partial \dot{q}_i}$$
(3.12)

Substituting (3.11) we derive

$$\frac{\partial V}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} = Q_i \tag{3.13}$$

These equations are derived for constant Q_i but they obviously apply for arbitrary time variations of Q_i since the rates \dot{q}_i of all state variables must depend only on the instantaneous configuration and forces.

Equations (3.13) are the fundamental equations for the time history of the thermodynamic system, under the external forces, Q_i . We have derived them in less detail in [1] and [2]. In these same papers we also derived a number of important properties which are straightforward consequences of (3.13) and which we now briefly describe.

The existence of normal coordinates follows from the existence of the quadratic invariants V and D. Relaxation modes satisfying orthogonality relations are derived from the corresponding eigenvalue problem. If the system is in the vicinity of stable equilibrium V is positive definite and all relaxation modes are proportional to an exponential time decay. If the system is unstable (e.g. under conditions of buckling) V is then indefinite and there exist modes proportional to increasing exponentials. The exponentials are always real because they correspond to eigenvalues of two quadratic forms one of which, D, is positive definite.

The dissipation function D is proportional to the entropy production and we have shown [2] that the instantaneous velocity vector \dot{q}_i of the system minimizes the entropy production for all vectors satisfying the condition that the power input of the disequilibrium forces

$$X_i = Q_i - \frac{\partial V}{\partial q_i}$$
 is constant i.e. if

$$X_i q_i = \text{const.} \tag{3.14}$$

An important expression is derived by considering a system in equilibrium under the forces $Q_i^{(s)}$. We may then write

$$\frac{\partial V}{\partial q_i} = Q_i^{(s)} \tag{3.15}$$

and from the properties of quadratic forms

$$V = \frac{1}{2} q_i Q_i^{(s)}$$
 (3.16)

This expression is convenient in practical applications to obtain V when relations such as (3.15) are known.

General expressions for the solutions of the fundamental equations in terms of the applied forces Q_i as given functions of time are easily obtained in operational form [1]. We write

$$q_i = A_{ij}^* Q_j \tag{3.17}$$

where $A_{ij}^* = A_{ji}^*$ is a symmetric admittance operator

$$A_{ij}^{*} = \sum_{j=1}^{(s)} \frac{C_{ij}^{(s)}}{p + \lambda_{s}} + C_{ij}$$
(3.18)

with p a time derivative operator

$$p = \frac{d}{dt} \tag{3.19}$$

and λ_s are characteristic roots of the differential equations (3.13) changed in sign. For a stable system the λ_s are real and non-negative. The diagonal coefficients $C_{ii}^{(s)}$ and C_{ii} are non-negative. The significance of the operational expression is a multiple one². In the case of forces which are simple harmonic functions of time, say $Q_i \exp(i\omega t)$ with a constant amplitude Q_i , the amplitudes q_i of the response $q_i \exp(i\omega t)$ are given by (3.18) after putting $p = i\omega$. Equations (3.18) may therefore be considered as relations between Fourier or Laplace transforms of Q_i and q_i . They may also be considered as integral expressions when the forces are arbitrary functions of time since we may write

$$\frac{p}{p+\lambda_s}Q_i(t) = e^{-\lambda_s t} \int_0^t e^{\lambda_s \tau} dQ_i(\tau) \qquad (3.20)$$

The reader's attention is called to the advantages of generality and flexibility attached to the use of the operational notation throughout.

Important relations of the impedance type are derived if we introduce the concept of "hidden coordinates." The thermodynamic system is considered as a "black box" with a large number of coordinates which are unobserved q_s . Perturbations (i.e. forces) are only applied to observed coordinates q_i while the forces applied to the hidden coordinates q_s are zero. A model for this is a large resistance-capacity network with certain numbers of outlet terminal pairs. We are interested in the relations between the applied forces Q_i and the compounding observed coordinates q_i . This introduces the impedance matrix of the thermodynamic system. We have shown [1] that

$$Q_i = Z^*_{\ ij} q_i \tag{3.21}$$

where $Z_{ij}^* = Z_{ji}^*$ is a symmetric impedance operator

$$Z_{ij}^{*} = \sum_{p=1}^{s} \frac{p}{p+r_{s}} D_{ij}^{(s)} + D_{ij} + D_{ij}^{(s)} p \qquad (3.22)$$

The relaxation constants r_s and all diagonal terms $D_{ii}^{(s)}$, D_{ii} , D_{ii}^{\prime} are non-negative. Expressions (3.20) and (3.22) are completely general and are valid whether the matrices of the original differential equations are singular or not or whether they have any number of multiple characteristic roots. Attention is called to the fact that in the derivation of (3.22), [1], we must invoke the non-negative character of the dissipation function otherwise a term in p^2 would appear in that expression.

A very useful variational principle equivalent to the Lagrangian equations (3.13) is obtained by introducing an operational form of the dissipation function

$$D^* = \frac{1}{2} p b_{ij} q_i q_j \tag{3.23}$$

We may then write the variational principle as

$$\delta V + \delta D^* = Q_i \delta q_i \tag{3.24}$$

This principle will be used later and also generalized in Section 7.

Thermoelasticity

An excellent illustration of the new methods and principles presented above is provided by their application to Thermoelasticity as we have already pointed out in [1] and [2] and developed more explicitly in the later papers [3] and [17].

It should be understood that the word Thermoelasticity is used here in its broadest meaning and embraces as particular cases the classical theory of Elasticity, the effect of temperature distribution on thermal stresses in elastic bodies, the theory of heat conduction and heat transfer and the coupled interaction between the deformation and the temperature field which results in thermoelastic damping.

The subject of Thermoelasticity has been the object of well known discussions in the literature for over a century among others by Duhamel [18], Neumann [19] and Voigt [20]. Duhamel's equations which were reproduced by Neumann are not based on thermodynamic principles and are restricted to isotropy. They are based on the experimentally known difference between the two specific heats. Thermoelastic damping was studied extensively both theoretically and experimentally by Zener [21], [22], [23], [24]. The present treatment brings all these phenomena into the general frame of linear thermodynamics and its variational treatment as outlined above. In addition it leads to new concepts and methods, in particular to the concepts of thermoelastic potential, a general dissipation function which includes surface heat transfer, and a thermal force defined by a method of virtual work in analogy with mechanics. Finally, as we have shown in [17], which deals specifically with the heat transfer aspects of the theory, the methods are susceptible of considerable extension beyond the scope of the present outline to include non-linear phenomena and new procedures of numerical analysis.

The concept of thermoelastic potential which we have proposed is entirely different from the expression used by Päsler [25] and which has been *mistakenly* referred to as a thermoelastic potential. Not only is the expression essentially different from ours, but the temperature plays the singular role of a parameter not subject to variation leading to a theory which does not contain heat transfer processes in variational form and does not fit in the scheme of the present general thermodynamic formulation. The potential used by Päsler is expression (4.32) below

²For an introduction to operational methods see e.g. [15], [16].

and referred to by Voigt [10] as the first thermodynamic potential.

The classical equations for the coupled elastic and thermal fields are

$$\sigma_{\mu\nu} = C^{ij}_{\mu\nu} e_{ij} - \beta_{\mu\nu}\theta$$
$$\frac{\partial \sigma_{\mu\nu}}{\partial x_{\mu}} = 0$$
(4.1)

$$\frac{\partial}{\partial x_i} \left[k_{ij} \frac{\partial \theta}{\partial x_j} \right] = c \frac{\partial \theta}{\partial t} + T_r \beta_{ij} \frac{\partial e_{ij}}{\partial t}$$

The stress tensor is $\sigma_{\mu\nu}$, the strain is

$$e_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$
(4.2)

and θ is the excess temperature above the reference temperature T_{r} . The thermal conductivity tensor is k_{ij} , c is the specific heat per unit volume, for zero strain, β_{ij} is related to the thermal dilatation properties of the material, and $C^{ij}_{\mu\nu}$ are the elastic moduli for *isothermal* deformations ($\theta = 0$). We have the following symmetry properties

$$C_{\mu\nu}^{ij} = C_{ij}^{\mu\nu} = C_{\nu\mu}^{ij} = C_{\mu\nu}^{ji}$$

$$\beta_{ij} = \beta_{ji}$$

$$k_{ij} = k_{ji}$$

(4.3)

The latter is only true in the absence of a strong magnetic field or Coriolis forces, as a consequence of Onsager's relations. Experimental confirmation of the symmetry of k_{ii} was found by Voigt [11].

A rederivation of the classical equations (4.1) may be found in the introductory part of [3] or in [27].

Thermoelastic phenomena obviously must obey the laws of linear thermodynamics. We have shown [3] that they obey the general variational formulation represented by the principle of minimum dissipation and the corresponding Lagrangian equations (3.13).

In order to show this we must of course choose the variables which define the thermodynamic state of the systems and correspond to the coordinates q_i of the general theory. The coordinate system chosen is the field of displacement vectors \overline{u} of the solid and in addition the vector field \overline{S} of entropy displacement. The vector \overline{S} is the time integral of the rate of heat flow divided by T_r . In this choice we are guided by expression (3.8). Hence,

$$\frac{\partial \overline{S}}{\partial t} = \frac{1}{T_r} \frac{\partial \overline{H}}{\partial t}$$
(4.4)

where $\partial H/\partial t$ is the rate of heat flow.

With the vector \overline{S} the classical equations (4.1) may also be put in an equivalent form by writing

$$\sigma_{\mu\nu} = C^{ij}_{\mu\nu} e_{ij} - \beta_{\mu\nu}\theta$$

$$\frac{\partial \sigma_{\mu\nu}}{\partial x_{\mu}} = 0$$

$$k_{ij} \frac{\partial \theta}{\partial x_{j}} = -T_{r} \frac{\partial S_{i}}{\partial t}$$

$$T_{r} div \overline{S} = -c\theta - T_{r}\beta_{ij} e_{ij}$$
(4.5)

The components of \overline{S} are designated by S_i . The third equation expresses the law of heat conduction while the fourth is derived from the thermostatic definition of entropy [3] assumed to be valid for non-equilibrium phenomena following the assumptions of linear thermodynamics (Section 2).

Let us evaluate the generalized free energy V. According to (2.19) this may be written

$$V = V_r + \frac{1}{2} \iiint_{\tau} \frac{c\theta^2}{T_r} dr$$
(4.6)

The isothermal free energy V is nothing but the well known isothermal strain energy of the classical theory of Elasticity.

$$V_r = \iiint_{\tau} W \, d\tau \tag{4.7}$$

where

$$W = \frac{1}{2} C_{\mu\nu}^{ij} e_{ij} e_{\mu\nu}$$
(4.8)

and $C^{ij}_{\mu\nu}$ are the isothermal elastic moduli.

$$V = \iiint_{\tau} \left(\mathbf{W} + \frac{1}{2} \frac{c\theta^2}{T_r} \right) d\tau \qquad (4.9)$$

This is the particular form assumed by the generalized free energy [3]. Since it embodies completely the thermostatic and elastic properties of the systems we have referred to expression (4.9) as the *thermoelastic potential*. Substituting the value of θ derived from (4.5) we express this thermoelastic potential in terms of the fields \overline{u} and \overline{S} as follows.

$$V = \iiint_{\tau} \left[\mathbf{W} + \frac{T_r}{2c} (div\,\overline{S} + \beta_{ij}\,\boldsymbol{e}_{ij})^2 \right] d\tau \quad (4.10)$$

The dissipation function is easily found by using its definition (2.9) in terms of entropy production. We found [3] [17],

$$D = \frac{1}{2} T_r \iiint_{\tau} \lambda_{ij} \frac{\partial S_i}{\partial t} \frac{\partial S_j}{\partial t} d\tau + \frac{1}{2} T_r \iint_{A} \frac{1}{K} \left(\frac{\partial S_n}{\partial t}\right)^2 dA \quad (4.11)$$

In this expression the matrix of λ_{ij} is the thermal resistivity matrix i.e. the inverse of the conductivity matrix k_{ij}

$$[\lambda_{ij}] = [k_{ij}]^{-1} \tag{4.12}$$

The first integral is proportional to the entropy production inside the system. The second integral taken over the boundary A of the system corresponds to the entropy production in the heat transfer layer at the boundary. The heat transfer coefficient at the boundary is denoted by K and S_n is the normal component of \overline{S} at the boundary. We may also use the alternate operational definition of the dissipation function following (3.23) and write

$$D^* = \frac{1}{2} p T_r \iiint_{\tau} \lambda_{ij} S_i S_j d\tau + \frac{1}{2} T_r \iint_{K} S_n^2 dA$$
(4.13)

Finally we must evaluate what corresponds to the generalized virtual work $Q_i \delta q_i$ in the general variational relation (3.24). This is the work performed on the system by the "externally" applied forces and temperatures. Here we must point out that while the force \overline{F} is applied to the solid boundary, the "external" temperature θ_a is that existing *outside* the heat transfer layer at the boundary. The generalized virtual work is the surface integral

$$Q_i \delta q_i = \iint_A \left(\overline{F} \cdot \delta \overline{u} + \theta_a \, \delta S_n \right) dA \tag{4.14}$$

where S_n is the normal component of \overline{S} at the boundary directed *positively inward*³. The variational principle corresponding to (3.24) is then

$$\delta V + \delta D^* = \iint_A \left(\overline{F} \cdot \delta \overline{u} + \theta_a \, \delta S_n \right) dA \qquad (4.15)$$

where V is the thermoelastic potential (4.10) and D^* the operational dissipation function (4.13). This relation must be verified for all variations of the fields \overline{u} and \overline{S} and as we have shown [3] [17] this leads to the classical equations in the form (4.5) for the thermoelastic field including the boundary conditions in the heat transfer layer. Conversely, the variational principle (4.15) also follows from (4.5). Hence if these equations are taken to represent experimentally verified laws of elasticity and heat conduction then the variational equation (4.15) is also true independently of the assumptions peculiar to linear thermodynamics. In particular they will be true without having to assume $\theta \ll T_r$. This is valuable in heat conduction when the methods and principles then become applicable for variations of θ in a large range [17].

The variational principle makes it possible to express the thermoelastic equations for homogeneous or inhomogeneous bodies, isotropic or anisotropic, in any system of curvilinear or generalized coordinates. If we use generalized coordinates q_i we may describe the fields \overline{u} and \overline{S} in terms of fixed configurations \overline{u}_i and \overline{S}_i . We write,

$$\overline{u} = \overline{u}_i q_i \quad \overline{S} = \overline{S}_s q_s \tag{4.16}$$

The set of generalized coordinates is q_i and q_s . As we have shown [3] the differential equations for these coordinates may then be written in the form (3.13) as

$$\begin{bmatrix}
\underline{M_{11}} & \underline{M_{12}} \\
\underline{M_{12}} & \underline{M_{22}}
\end{bmatrix}
\begin{bmatrix}
q_i \\
q_s
\end{bmatrix}
+
\begin{bmatrix}
0 & 0 \\
0 & N
\end{bmatrix}
\begin{bmatrix}
\dot{q}_i \\
\dot{q}_s
\end{bmatrix}
=
\begin{bmatrix}
Q_i \\
Q_s
\end{bmatrix}$$
(4.17)

with partitioned matrices, Q_i representing the mechanical forces and Q_s the thermal forces (M'_{12}) is the transpose of M_{12}). We may restrict ourselves to applying a certain number of mechanical forces Q_i and observe the corresponding coordinates q_i (q_s being "hidden"), all other forces being zero. We may then write

$$Q_i = Z_{ij}^* q_j \tag{4.18}$$

with a thermoelastic impedance

$$Z_{ij}^{*} = \sum_{p=1}^{s} \frac{p}{p+r_{s}} D_{ij}^{(s)} + D_{ij}$$
(4.19)

This expression is a particular case of (3.22) and may be derived by following the general procedure which we used in [1]. They are a consequence of the particular nature of the matrices in (4.17). In the derivation use must be made of the fact that the generalized free energy is non-negative.

An important property of thermoelastic systems is derived from (4.17). Eliminating q_i by matrix multiplication yields

$$[M_{22} - M_{12}'M_{11}^{-1}M_{12}]q_s + N\dot{q}_s = Q_s - M_{12}'M_{11}^{-1}Q_i \quad (4.20)$$

³An additional term for body forces may be added as done in [3].

Since the matrices multiplying q_s and \dot{q}_s are symmetric this may be considered to represent a pure relaxation phenomenon for the entropy field. The entropy therefore obeys quite generally diffusion type equations. This may be verified directly in the case of a homogeneous isotropic body. In this case the stress-strain law is⁴

$$\sigma_{ij} = 2 \mu e_{ij} + \delta_{ij} (\lambda e - \beta \theta)$$

$$(e = \delta_{ij} e_{ij})$$
(4.21)

and the thermal conductivity is

$$k_{ij} = \delta_{ij} k \tag{4.22}$$

We have shown [3] that the entropy per unit volume or specific entropy

$$s = -div\bar{S} \tag{4.23}$$

satisfies the diffusion equation

$$\frac{k}{c} \frac{2\mu + \lambda}{\left(2\mu + \lambda + \beta^2 \frac{T_r}{c}\right)} \nabla^2 s = \frac{\partial s}{\partial t} \qquad (4.24)$$

This means that if we suddenly deform an isotropic elastic body the specific entropy does not initially vary inside. It remains constant until it has had time to change by diffusion from the boundaries. It is interesting to interpret this in terms of the analogy which we have demonstrated to exist between thermoelasticity and the isothermal mechanics of elastic porous media containing a viscous compressible fluid [3]. The specific entropy plays the role of what we have called the fluid content ζ [28] [30]. When we suddenly form such a porous body there is generally an instantaneous flow of the fluid but there is at first no change in fluid content ζ inside the body until it diffuses from the boundaries. Complete isomorphism exist between the two theories and the general solutions of the equations of consolidation of porous media of reference [28] apply to thermoelasticity and the evaluation of thermal stresses by a simple change in notation. The isomorphism is a consequence of the fact that both phenomena obey the same basic thermodynamic principles.

It is of considerable interest to point out that for isotropic bodies the thermal conductivity as expressed by (4.22) automatically satisfies Onsager's relations purely on the basis of *geometric symmetry*.

We shall add a remark concerning the significance of the thermoelastic potential (4.9). Its specific value per unit volume is the integrand in (4.9) i.e.

$$v = W + \frac{1}{2} \frac{c\theta^{2}}{T_{r}} = W + \frac{T_{r}}{2c} (\beta_{ij} e_{ij} - s)^{2} \qquad (4.25)$$

This may be written

or

$$v = \frac{1}{2}\sigma_{ij}e_{ij} + \frac{1}{2}\theta s \qquad (4.26)$$

an expression identical in form with (3.16) of the general theory. For adiabatic deformations we must put s = 0 and the generalized free energy becomes

$$v = W + \frac{T_r}{2c} (\beta_{ij} e_{ij})^2$$
 (4.27)

 $v = \frac{1}{2} \left[C_{\mu\nu}^{ij} + \frac{T_r}{c} \beta_{ij} \beta_{\mu\nu} \right] e_{ij} e_{\mu\nu} \qquad (4.28)$

This represents the elastic strain energy for adiabatic deformations and the expressions in the bracket are the *adiabatic elastic moduli*. They are derived here very simply from the generalized free energy. The same procedure may be used to derive the adiabatic compliance coefficients. It is interesting to compare (4.26) with the concept of thermodynamic potential which in case the stress is a hydrostatic pressure p, is u - sT + pe. Generalized to the stress tensor this is written⁵

$$\zeta = u - sT - \sigma_{ij} e_{ij} \tag{4.29}$$

In our notation with $T = T_r + \theta$ it becomes

$$\zeta = u - sT_r - s\theta - \sigma_{ij}e_{ij} \qquad (4.30)$$

Taking into account (2.13) and (4.26) we find

$$\zeta = -v \tag{4.31}$$

The quantity ζ is mentioned by Voigt [20] who refers to it as the second thermodynamic potential. Although it differs only in sign from our generalized free energy it is a very different physical concept, which refers only to isothermal properties at the temperature $T = T_r + \theta$. Voigt also considers the classical isothermal free energy

$$\xi = u - s \left(T_r + \theta \right) = W - \frac{1}{2} \frac{c\theta^2}{T_r} - \theta \beta_{ij} e_{ij} \qquad (4.32)$$

which he refers to as the first thermodynamic potential. Expression (4.32) was used by Päsler [25].

 $^{^{4}\}lambda$ and μ are the isothermal Lamé constants. From (4.28) the adiabatic Lamé constants are $\lambda + \beta^2 T_{r/c}$ and μ .

⁵u is the internal energy per unit volume.

Thermoelastic Dissipation

When Thermoelasticity is coupled with dynamics the difference arises in the addition of an acceleration term in the second equation in (4.1) and (4.5). i.e.

$$\frac{\partial \sigma_{\mu\nu}}{\partial x_{\mu}} = \rho \ \frac{\partial^2 u_{\nu}}{\partial t^2} \tag{5.1}$$

where ρ is the mass density. As we have shown [3] this leads to a Lagrangian formulation of the problem with a kinetic energy

$$T = \frac{1}{2} \iiint_{\tau} \rho \left(\frac{\partial u_i}{\partial t}\right)^2 d\tau = \frac{1}{2} m_{ij} \dot{q}_i \dot{q}_j \qquad (5.2)$$

The differential equations for the system then become

$$\frac{\partial V}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_i} \right) = Q_i$$
 (5.3)

An operational kinetic energy may also be introduced

$$T^* = \frac{1}{2} p^2 \iiint_{\tau} \rho u_i^2 dt = \frac{1}{2} p^2 m_{ij} q_i q_j$$
(5.4)

with the corresponding Lagrangian equations

$$\frac{\partial}{\partial q_i} \left(V + D^* + T^* \right) = Q_i \tag{5.5}$$

The equations may be put in an interesting form if we separate the coordinates as in (4.17) into mechanical ones q_i and purely thermal ones q_s . In addition, we assume that the only forces applied are mechanical forces Q_i . The thermal variables q_s may then be considered as "hidden." Moreover, using d'Alembert's principle we may introduce a force

$$Q'_{i} = -\frac{d}{dt} \frac{\partial T}{\partial q_{i}} + Q_{i}$$
(5.6)

and express the forces Q'_i in terms of q_i by means of the thermoelastic impedance (4.19). We find

$$Q'_{i} = \left[\sum_{j=1}^{s} \frac{p}{p+r_{s}} D_{ij}^{(s)} + D_{ij}\right] q_{j}$$
(5.7)

Substituting in (5.6) the equations of the system become

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) + \left[\sum_{i=1}^{s} \frac{p}{p+r_s} D_{ij}^{(s)} + D_{ij}\right] q_j = Q_i \quad (5.8)$$

In the case of harmonic oscillations $(p = i\omega)$, the coefficients in the bracket may be considered as complex frequency-dependent moduli. There is a spectrum of relaxation constants r_s . The imaginary part of each component of the spectrum is

$$lm \ \frac{p}{p+r_s} = \frac{\omega r_s}{r_s^2 + \omega^2}$$
(5.9)

It represents the damping and goes through a maximum for a frequency,

$$\omega = r_s \tag{5.10}$$

A simple example of a vibrating rod is treated by this method in [3]. The more complex problem of thermoelastic dissipation of an inhomogeneous polycrystalline solid, which was already analyzed by Zener [22] may be given a simple and systematic treatment by the present methods.

We have pointed out [3] that wave propagation in a thermoelastic medium obeys exactly the same equations as those of wave propagation in a porous solid saturated with a massless fluid which we developed in detail for the isotropic case [30]. The shear wave is unattenuated and is the same as in the classical purely elastic theory. We derived [3] [30] the equations for the dilatational wave

$$\left(\lambda + 2\mu + \frac{\beta^2 T_r}{c}\right) \nabla^2 e - \frac{\beta T_r}{c} \nabla^2 s = \rho \frac{\partial^2 e}{\partial t^2}$$

$$- \frac{\beta T_r}{c} \nabla^2 e + \frac{T_r}{c} \nabla^2 s = \frac{T_r}{p} \frac{\partial s}{\partial t}$$
(5.11)

This form of the equations brings out the symmetry of the coefficients. From the porous medium analogy [30], we conclude readily that there are two dilatational waves. However, because of the smallness of the coupling term $\beta T_r/c$ the wave of the "first kind" is a slightly attenuated sound wave while the wave of the "second kind" is a highly attenuated almost pure heat diffusion process.

The propagation is the same as in the acoustics of a gas where it is well known that waves of the first kind become isothermal in the limit of high frequency [31].

A point of interest with respect to thermoelastic dissipation is to evaluate the magnitude of the dissipated power. As before, we separate the variables into mechanical and purely thermal variables q_i , q_s , respectively. The thermal forces Q_s applied externally are assumed to be zero ($\theta_a = 0$). The mechanical forces are designated by Q_i and the equations for the system are separated into two groups

$$\frac{\partial V}{\partial q_i} + \frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_i} \right) = Q_i$$

$$\frac{\partial V}{\partial q_s} + \frac{\partial D}{\partial \dot{q}_s} = 0$$
(5.12)

multiplying the first equations by \dot{q}_i and the second by \dot{q}_s and adding, we obtain

$$\frac{d}{dt}(V+T) + 2D = Q_i \dot{q}_i$$
(5.13)

The right hand side represents the power input of the mechanical forces. On the left the term 2D equal to twice the dissipation function is non-negative and represents the irreversible conversion of mechanical power into heat. This dissipation function D is given by (4.11). This heat generation produced by the dissipation is a quantity of the *second order* which in a first order theory is neglected in comparison with the *first order* entropy flow vector \overline{S} as defined above. Over a certain period of time this second order heat may of course accumulate and if not diffused out will produce an increase of temperature comparable to first order effects. A direct verification of the conversion of the dissipated power into heat is obtained by writing the first law of thermodynamics in the form

$$-\frac{dh}{dt} = -\frac{du}{dt} + \sigma_{ij} \frac{de_{ij}}{dt}$$
(5.14)

where $-\frac{dh}{dt}$ is the heat exuded per unit volume and unit time and u is the internal energy per unit volume. Replacing $\sigma_{\mu\nu}$ by its expression from the equation of state i.e. the first equation (4.5); further, using the last

equation (4.5) and introducing the value v from (4.26) we find,

$$-\frac{dh}{dt} = -\frac{d}{dt}(u-v) + \theta \, div \left(\frac{\partial \overline{S}}{\partial t}\right) \tag{5.15}$$

The irreversible part of the power is obviously contained in the second term. A simple calculation gives the volume integral of this second term as

$$\iiint_{\tau} \theta \, div \left(\frac{\partial \overline{S}}{\partial t}\right) d\tau = 2 D \qquad (5.16)$$

where D is given by (4.11). In order to establish this last relation we integrate by parts and introduce the assumption that the externally applied temperature θ_a is zero ($Q_s = 0$). Hence in that case 2D represents the total heat exuded irreversibly from the volume.

Viscoelasticity

Viscous and relaxation phenomena in the linear range may in general be assumed to obey the thermodynamic equations formulated above. Strictly speaking of course we must deal with a system which is initially in equilibrium and undergoing small disturbances from this state. Actually we may expect the equations in certain specific cases to be verified in a much wider range while in some other instances non-linearities will appear even for physically very small disturbances. Furthermore because of their wide validity the thermodynamic principles lead to expression which in many cases give a first approximation to the physical properties in the same sense that Hooke's law in Elasticity yields a widely valid approximation to the actual properties of materials. In this connection and as already pointed out in Section 1 we should remember that linearity does not insure the validity of Onsager's relations as they do not necessarily apply in the presence of a magnetic field or a field of Coriolis forces. However, in practice the actual restrictions of this type to the validity of the equations will appear only in exceptional cases.

Application of Onsager's relations to viscoelasticity were made by Staverman and Schwarzl [32] [33] and Meixner [34] [35]. Simultaneously a very general approach to viscoelasticity based on linear thermodynamics as presented here was developed by this writer [1] [2].

Our treatment appears to be more general since, as illustrated in the case of thermoelasticity (Section 4), it includes heat conduction as a particular case and the coupling of thermomechanical effects with physicochemical, electrical, and other thermodynamic degrees of freedom⁶. We also derived the general form of the operational moduli relating stress and strain and made it the object of a rigorous proof [1]. We subsequently included the treatment of a fluid-saturated porous viscoelastic anisotropic solids [36], and the application to the dynamics of viscoelastic structures of some variational principles which we had developed earlier for linear thermodynamics [2]. This leads to a variationaloperational method and to Lagrangian equations with operational coefficients [37] [38].

The operational relations between stress and strain are an immediate consequence of expressions (3.17) and (3.21). Consider an element of solid of unit volume. The nine stress components $\sigma_{\mu\nu}$ may be identified with the nine applied forces Q_i to the system and the nine components e_{ij} of the strain tensor are the corresponding

⁶It includes for instance as a particular case the theory of thermal stresses of viscoelastic media with temperature independent stressstrain relations. This is formally identical with the treatment of porous viscoelastic media [36].

observed coordinates q_i . The solid is assumed to contain hidden coordinates which may be finite or infinite in number. The strain is then expressed in terms of the stress by an operational compliance matrix $A^{*ij}_{\mu\nu}$ which corresponds to the general admittance (3.18).

$$e_{\mu\nu} = A^{*\,ij}_{\mu\nu}\,\sigma_{ij} \tag{6.1}$$

Solving the system for σ_{ij} brings out operational moduli which correspond to the impedance (3.22).

$$\sigma_{\mu\nu} = Z^{*\,ij}_{\mu\nu} e_{ij} \tag{6.2}$$

The operators are

$$A^{*\,ij}_{\mu\nu} = \int_0^\infty \frac{C^{ij}_{\mu\nu}(\lambda)}{p+\lambda} \, d\lambda + C_{ij} \tag{6.3}$$

$$Z^{*\,ij}_{\mu\nu} = \int_0^\infty \frac{p}{p+r} D^{ij}_{\mu\nu}(r) \, dr + D^{ij}_{\mu\nu} + p D^{\prime ij}_{\mu\nu} \tag{6.4}$$

The summations in expressions (3.18) and (3.22) are replaced by integrals. This of course is more convenient as an approximation if there are a great number of hidden coordinates. In doing so we must take care of the fact that $C_{\mu\nu}^{ij}(\lambda)$ and $D_{\mu\nu}^{ij}(r)$ may be highly discontinuous functions. These discontinuities are due to the fact that these functions include a spectral density factor for the relaxation constants λ and r and also because the coefficients $C_{ij}^{(s)}$ and $D_{ij}^{(s)}$ themselves in expressions (3.13) and (3.22) may be discontinuous functions of λ_s and r_s . The discontinuities may be of the Dirac function type. The discreet spectrum in expressions (3.18) (3.22) is included in the integral representations (6.3) (6.4) by the introduction of Dirac functions. Further properties of the operators (6.3) and (6.4) are

1. The operators satisfy the symmetry properties

$$A^{*ij}_{\mu\nu} = A^{*ij}_{\nu\mu} = A^{*ji}_{\mu\nu}$$

$$Z^{*ij}_{\mu\nu} = Z^{*ij}_{\nu\mu} = Z^{*ji}_{\mu\nu}$$
(6.5)

which are consequence of the symmetry of σ_{ij} and e_{ij}

2. In addition they satisfy the symmetry property

$$\begin{aligned} A^{*ij}_{\mu\nu} &= A^{*\mu\nu}_{ij} \\ Z^{*ij}_{\mu\nu} &= Z^{*\mu\nu}_{B^{*}} \end{aligned} \tag{6.6}$$

which is a consequence of the Onsager reciprocity relations.

3. The variables λ and r are real and non-negative. They are real because of Onsager's relations and the non-negative dissipation functions D. They are nonnegative because we have assumed the system to be disturbed in the vicinity of stable equilibrium, hence such that the generalized free energy V is non-negative.

4. All diagonal terms $C_{ij}^{ij}(\lambda)$, C_{ij}^{ij} , and $D_{ij}^{ij}(r)$, D_{ij}^{ij} , D_{ij}^{ij} are non-negative. This is also a consequence of Onsager's relations and the non-negative character of the generalized free energy and the dissipation function. This non-negative character of the diagonal terms is an invariant property which must be valid for all linear transformations of the six independent variables e_{ij} . It follows that the coefficients C and D must be such that $D_{\mu\nu}^{ij}(r) e_{ij} e_{\mu\nu}$, $D_{\mu\nu}^{ij} e_{ij} e_{\mu\nu}$, $D_{\mu\nu}^{ij}(\lambda) e_{ij} e_{\mu\nu}$, and $C_{\mu\nu}^{ij} e_{ij} e_{\mu\nu}$ are all non-negative quadratic forms.

As already mentioned above (Section 3), a more subtle point in deriving expression $Z^{*\,ij}_{\mu\nu}$ is that from a purely algebraic viewpoint there arises the possibility of an additional term $D^{\prime\prime ij}_{\mu\nu} p^2$ which would introduce a dependence on the strain acceleration. However, because we are dealing with a positive-definite dissipation function we were able to show [1] that the term in p^2 must vanish. This point is an important one and although it was introduced explicitly in [1] it was not given due emphasis.

We have assumed implicitly that the thermodynamic equations involve the hidden coordinates only in V and D. If this is not the case, i.e. if hidden coordinates appear also in the kinetic energy we still derive the symmetry properties 1 and 2 but the nature of the operators is affected by the possible introduction of complex conjugate quantities. This will also affect the nature of the heredity functions below (6.8)

We have written the above relations as operational equations. The reader is reminded of the significance of these equations. They may be considered as direct relations between the *Laplace transforms* of the time dependent functions. We may also introduce explicitly differential and integral operation represented by the operators in accordance with expressions (3.19) and (3.20). Hence the stress-strain relations (6.2) may be written as,

$$\sigma_{\mu\nu} = \int_0^t h_{\mu\nu}^{ij}(t-r) \, de_{ij}(r) + D_{\mu\nu}^{ij} + D_{\mu\nu}^{\prime ij} \, \frac{de_{ij}}{dt} \quad (6.7)$$

with an heredity tensor

$$h_{\mu\nu}^{ij}(t) = \int_0^\infty D_{\mu\nu}^{ij}(r) \, e^{-rt} \, dr. \tag{6.8}$$

The function $D_{\mu\nu}^{ij}(r)$ is a "spectral tensor" of the fourth rank. In this sense the spectrum depends on the particular choice of the coordinate system for representing the stress and the strain and on the particular constraints imposed on the system. We may manipulate (6.1) or (6.2) as if the coefficients were algebraic quantities and thus obtain the matrix relating any choice of stress components with the corresponding strain. The new operators of course are not obtained in the form (6.4). But it should always be possible to do so. If we call B(p) that part of the new operators which corresponds to the integrals in (6.3) and (6.4), the problem amounts to finding a function F(r) which satisfies the integral equation

$$B(p) = \int_0^\infty \frac{p}{p+r} F(r) \, dr. \tag{6.9}$$

A very simple solution for this integral equation was given by Fuoss and Kirkwood [39] in connection with problems of dielectric relaxation of polymers. A discussion of this integral equation in connection with one dimensional problems of viscoelasticity has been given by Gross [40]. The integral equation may be considered of course as a generalization of an expansion in partial fractions. Once we know F(r) the operator B(p) may be expressed immediately in terms of an heredity operator by following the procedure outlined above. We may write

$$B(p) = \int_0^t h(t-\tau) d$$

with

$$h(t) = \int_0^\infty F(r) \, e^{-rt} \, dr \tag{6.10}$$

As an example we can use this method to derive the moduli $Z^{*\,ij}_{\mu\nu}$ from the compliance matrix $A^{*\,ij}_{\mu\nu}$ and vice versa. One matrix is the inverse of the other

$$[Z_{\mu\nu}^{*\,ij}] = [A_{\mu\nu}^{*\,ij}]^{-1} \tag{6.11}$$

Then any term of the inverse matrix may be written in the form (6.4) by first separating the terms $D_{\mu\nu}^{ij} + p D_{\mu\nu}^{'ij}$ then representing the remainder in the spectral form by solving an integral equation of the type (6.9).

In the one dimensional case corresponding to a simple tension test the stress σ and the strain e are related by either

$$e = A^* \sigma$$

$$\sigma = Z^* e$$
(6.12)

where the compliance operator is

$$A^* = \int_0^\infty \frac{E(\lambda)}{p+\lambda} \, d\lambda + C \tag{6.13}$$

and the "operational Young's modulus" is

$$Z^* = \frac{1}{A^*} = \int_0^\infty \frac{p}{p+\lambda} F(r) \, dr + D + D'p \qquad (6.14)$$

These relations show that the material is represented by a model of springs and dashpots. Equations (6.12) and (6.13) correspond to two equivalent models which are respectively a Voigt model (Fig. 3) and a Maxwell model (Fig. 4). We can see that the possibility of representing the material by such models is a consequence of the Onsager relations and the non-negative character of the generalized free energy and the dissipation function.

It is of interest to point out how thermodynamics restricts the nature of the general type of operators which would otherwise result from a purely mathematical approach to linear theory. A general linear relation between stress and strain would read

$$\left[\sum_{\mu\nu}^{s} a_{\mu\nu}^{ij(s)} p^{s}\right] \sigma_{\mu\nu} = \left[\sum_{\mu\nu}^{s} b_{\mu\nu}^{ij(s)} p^{s}\right] e_{\mu\nu} \quad (6.15)$$

where $p = \frac{d}{dt}$ is again the time derivative. We could solve the system for $\sigma_{\mu\nu}$ and obtain a relation of the form

$$\sigma_{\mu\nu} = P^{*\,ij}_{\mu\nu} e_{ij} \tag{6.16}$$

where the elements of the matrix $P^{*ij}_{\mu\nu}$ are quotients of polynomials in p. Expanding these algebraic functions we shall obtain expression which are in general quite different from (6.4) because

1. The roots r of the denominator may be complex conjugates.

2. There may be terms in the expression of the type $1/(p+r)^n$ due to multiple roots.

3. The matrix is not in general symmetric except for isotropic media.

4. The diagonal terms may be negative.

5. Acceleration terms and higher order derivatives may be present.

For a thermodynamic system as we have already pointed out complex conjugate quantities may arise only if there are hidden coordinates with kinetic energy.

We have pointed out [1] [2] that an important consequence of the symmetry properties of the operational moduli is that they may be manipulated algebraically as elastic moduli. This establishes a rule by which the great generality of the equations of the classical theory of Elasticity may be immediately extended to Viscoelasticity by simply replacing the elastic moduli by their corresponding operators. We have also shown [2] [37] [38] that the property extends to the variational and energy methods replacing the strain invariants of the theory of Elasticity by their corresponding operational



FIGURE 3. VOIGT MODEL OF VISCOELASTICITY.

expressions. We have referred to this as the correspondence rule. An immediate application of this rule refers to properties of geometric symmetry [1]. An isotropic material will be characterized by two operators, cubic symmetry by three operators, transverse isotropy by five operators, and so on. We have pointed out that the frequency dependence of the operators leads to a property which does not occur in the theory of Elasticity i.e. that a material may change from one type of symmetry to another depending on the frequency range considered.

In general this correspondence rule is a consequence of the Onsager relations. However for an isotropic material this is not necessary since the geometric symmetry in this case insures the symmetry of the matrix of the moduli. The stress-strain relations in this case are

$$\sigma_{ij} = 2 Q^* e_{ij} + \delta_{ij} R^* e$$

$$(e = \delta_{ij} e_{ij})$$
(6.17)

with two distinct operators

$$Q^{*} = \int_{0}^{\infty} \frac{p}{p+r} Q(r) dr + Q + pQ'$$
(6.18)
$$R^{*} = \int_{0}^{\infty} \frac{p}{p+r} R(r) dr + R + pR'$$

corresponding to the Lamé constants μ and λ . However, the particular form above of the operators Q^* and R^* are a consequence of thermodynamics and not of the isotropy.

A restricted form of correspondence has been known for the incompressible isotropic case (41) (42) and has been referred to sometimes as the "viscoelastic analogy." The general correspondence rule in the context of thermodynamics for both isotropic and anisotropic media was first formulated by this writer [1]. For the isotropic case it is clearly independent of Onsager's relations since geometric symmetry alone implies that the compliance matrix is diagonal. We further developed its corrollary, an operational-variational principle and other applications [37] [38] (see Section 7). We have also extended the correspondence rule to isotropic and anisotropic porous viscoelastic media [36]. In this case Onsager's relations are required even in the isotropic case.



FIGURE 4. MAXWELL MODEL OF VISCOELASTICITY.

As mentioned above the term Viscoelasticity is used here in a very broad sense to include all viscous and relaxation phenomena including thermoelasticity. One might ask, therefore, how the operational stress-strain relations (6.1) (6.2) written above are related to the treatment of Thermoelasticity in Sections 4 and 5. The difference lies in the fact that in the present Section we have considered the strain to be the only relevant observed coordinate of the material element. The stressstrain relations (6.1) (6.2) are valid for Thermoelasticity and correspond to hidden coordinates which represent thermal changes inside an inhomogeneous polycrystalline material. Other hidden degrees of freedom would be represented for instance by viscous slip at intergrain boundaries or by the phenomenon of solution and recrystallization due to local stresses and the corresponding associated diffusion process.

Dynamics and Stress Analysis of Viscoelastic Structures

For "small" oscillations it may be expected that many engineering structures obey linear viscoelastic laws. This has been observed not only in continuous solids but also in riveted structures such as bridges and aircraft frames. Recent vibration tests of granular materials by Duffy and Mindlin [43] also indicate properties closer to a linear relaxation process rather than a Coulomb type friction.

The dynamics and stress analysis of viscoelastic structures may be conveniently carried out by using generalized coordinates. As we have shown [2] [19] [20] an important aspect of the correspondence rule is the possibility of introducing an *operational-variational* method. We mean by this the use of a variational method on invariants with operational coefficients. The operational invariant which corresponds to the elastic strain energy is

$$J^{*} = \frac{1}{2} \iiint_{\tau} Z^{*\,ij}_{\mu\nu} e_{\mu\nu} e_{ij} d\tau \qquad (7.1)$$

The invariant corresponding to the kinetic energy has already been introduced above as

$$T^* = \frac{1}{2} p^2 \iiint_{\tau} \rho u_i^2 d\tau \tag{7.2}$$

As we have shown [2] [37] [38], if we represent the deformation field by generalized coordinates q_i we obtain the equations for q_i by writing the variational principle

$$\delta J^* + \delta T^* = Q_i \delta q_i \tag{7.3}$$

where the right-hand side represents the virtual work of all forces applied externally to the system. This leads to Lagrangian equations in operational form

$$\frac{\partial}{\partial q_i} (J^* + T^*) = Q_i \tag{7.4}$$

Explicitly the equations are

$$(Y_{ij}^* + p^2 m_{ij}) q_j = Q_i$$
 (7.5)

In general the theorem of Fuoss and Kirkwood will be applicable leading to a spectral representation of the operator as

$$Y_{ij}^{*} = \int_{0}^{\infty} \frac{p}{p+r} F_{ij}(r) dr + Y_{ij} + Y_{ij}' p \qquad (7.6)$$

This operator is equivalent to the integro-differential operations

$$Y_{ij}^{*} q_{j} = \int_{0}^{t} h_{ij}(t-\tau) dq_{j}(\tau) + Y_{ij} + Y_{ij}' \frac{dq_{j}}{dt} \quad (7.7)$$

with the heredity functions

$$h_{ij}(t) = \int_0^\infty e^{-rt} F_{ij}(r) \, dr \tag{7.8}$$

Equations (7.5) therefore represent a generalization of Lagrange's equations to integro-differential form.

The function $h_{ij}(t)$ will be of the form (7.8) if Onsager's relations are applicable but it may also be of a more general form since the operator is defined as Laplace transforms independently of any thermodynamics. Furthermore the variational method above is valid for isotropic media and in that case is also not dependent on thermodynamics.

An interesting case in the dynamics of structures is when the operators $Z^{*ij}_{\mu\nu}$ may be written,

$$Z^{*\,ij}_{\mu\nu} = C^{ij}_{\mu\nu} f^* \tag{7.9}$$

where f^* is an invariant operator and $C^{ij}_{\mu\nu}$ are constants which may depend on the location. We have referred to this as the case of an homogeneous spectrum [38]. In this case the invariant J^* becomes

$$J^{*} = \frac{1}{2} f^{*} \iiint_{\tau} C^{ij}_{\mu\nu} e_{\mu\nu} e_{ij} d\tau \qquad (7.10)$$

With normal coordinates q_i the two quadratic forms appearing in J^* and T^* may be reduced to a sum of squares

i.e. we may write

$$J^{*} = \frac{1}{2} f^{*} \omega_{i}^{2} q_{i}^{2}$$

$$T^{*} = \frac{1}{2} p^{2} q_{i}^{2}$$
(7.11)

and the operational Lagrangian equations reduce to *independent* equations

$$f^* \omega_i^2 q_i + p^2 q_i = Q_i \tag{7.12}$$

We have referred to such modes as *partial modes* [37]. They may be calculated by the same method as in the usual vibration analysis of elastic structures. All modes have the same relaxation spectrum.

The same property extends to cases where the materials are not necessarily represented by operators of the type (7.9). Actually it is sufficient that for some reason the invariant J^* contain a single operator coefficient. Such is the case for instance for an isotropic incompressible material. In this case variations must be constrained by the condition of incompressibility. Moreover, if there are boundary constraints they must be such that no work is done, i.e. they are either free of stress or have no displacement. In general this will be accomplished if the deformation is constrained in such a way that a single operator may be factorized. Such is the case for instance in the bending of a thin rod with end conditions either clamped, pinned, or free. The invariant J^* in that case contains only a single operator E^* . We write

$$J^* = \frac{1}{2} E^* \int l \left(\frac{\partial^2 w}{\partial x^2} \right)^2 dx \qquad (7.13)$$

where w is the deflection of the rod as a function of the coordinate x and I the cross-section moment of inertia. The operator E^* is obtained from the expression of Young's modulus in terms of the Lamé constants and replacing the latter by R^* and Q^* in accordance with the correspondence rule.

We find

$$E^* = \frac{Q^*(3R^* + 2Q^*)}{Q^* + R^*} \tag{7.14}$$

We may, therefore, analyze the bending vibrations of such a viscoelastic rod by the use of normal coordinates and for ends which are free, clamped, or pinned. The same separation in normal coordinates may of course be accomplished if the structure is composed of elements of homogeneous material in which a rod type bending and elongation is the predominant deformation. If we neglect the inertia forces a structure composed of an isotropic material may be analyzed by normal coordinates since the invariant is separated into two terms each multiplied by a different operator.

$$J^* = \frac{1}{2} \iiint [2Q^* e_{ij} e_{ij} + R^* e^2] d\tau \qquad (7.15)$$

This constitutes the generalization of a procedure suggested by Cosserat about sixty years ago for elastic systems [44].

We shall end with a short remark on the nature of solid friction. In problems of flutter analysis of aircraft structures it has been customary to take care of the solid friction by replacing the rigidity moduli by complex frequency-independent quantities. This may be approximated in the above representation if we put

$$F_{ij}(r) = \gamma_{ij}/r \quad r > \epsilon$$

$$F_{ij}(r) = 0 \quad r < \epsilon$$
(7.16)

Expression (7.6) then becomes (with $p = i\omega$)

$$Y_{ij}^{*} = \int_{\epsilon}^{\infty} \frac{i\omega}{i\omega + r} \frac{\gamma_{ij}}{r} dr + Y_{ij}$$
$$Y_{ij}^{*} = i\left(\frac{\pi}{2} - \tan^{-1}\frac{\epsilon}{\omega}\right) \gamma_{ij} + \gamma_{ij}\log \sqrt{1 + \frac{\omega^{2}}{\epsilon^{2}}} + Y_{ij}$$
(7.17)

For a small value of ϵ and γ_{ij} the complex Y_{ij}^* is almost constant for a wide range of frequency.

The correspondence rule and the operational-variational principle are applicable to a very wide category of practical problems. We have shown in [37] and [38] how they lead to general methods in problems of dynamics and stress analysis of viscoelastic plates and shells even in *non-linear problems* of finite deflections. In problems of *thermal stresses* in elastic and viscoelastic structures, applications of the principles developed above has led to new concepts and methods. We have shown that a direct calculation of thermal stresses is possible which avoids the necessity of first calculating the temperature field [45]. The analysis can be carried out entirely by variational procedures.

Acknowledgements

This work was sponsored jointly by the Shell Development Company and the Cornell Aeronautical Laboratory. Sections 2 and 3 are based on lectures delivered by this writer at the Emeryville Laboratory of the Shell Development Co. in February 1955. 1. Biot, M. A., "Theory of Stress-Strain Relations in Anisotropic Viscoelasticity and Relaxation Phenomena," *Jour. Applied Phys.*, Vol. 25, No. 11, pp. 1385-1391, 1954.

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