Irreversible thermodynamics with internal inertia.
Principle of stationary total dissipation

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THE NOTION of "internal inertia" is introduced and discussed. The existence of entropy is proved in the presence of internal inertia. A new thermodynamic function called the Lagrangian density is introduced and its importance in deriving internal constitutive equations is shown. The principle of stationary total dissipation is established and discussed.

Wprowadzono i przedyskutowano pojęcie wewnętrznej bezwładności. Udowodniono istnienie entropii dla przypadku, kiedy obecna jest wewnętrzna bezwładność. Wprowadzono nową funkcję termodynamiczną nazywaną gęstością Lagrange'a i pokazano jej znaczenie przy wyprowadzaniu wewnętrznych równań konstytutywnych. Ustanowiono i przedyskutowano zasadę stałości całkowitej dysypacji.

Выведено и обсуждено понятие внутренней инерции. Доказано существование энтропии в случае, когда имеется внутренняя инерция. Вводится новая термодинамическая функция, именуемая плотностью Лагранжа. Показано её значение при выводе внутренних определяющих уравнений. Сформулирован и исследован принцип стационарности полной диссипации.

1. Introduction

IN THIS paper we have introduced a number of concepts and presented results that are new to the theory of irreversible thermodynamics. The notion of "internal inertia" is introduced and discussed; the existence of entropy which we demonstrated in a previous paper [1] is proved also in the presence of internal inertia; a new thermodynamic function, which we call the Lagrangian density because of its resemblance in form to the Lagrangian of classical mechanics, is introduced and its importance in deriving "internal constitutive equations" is shown. Finally, with the aid of the above ideas we have established the Principle of Stationary Total Dissipation, which we discuss in detail in the text.

The thermodynamics of dissipative thermomechanical systems, which is based on the theory of internal variables, has been laid on sound foundations and appears to offer by far the best avenue of ever bridging the chasm that separates continuum and microscopic physics. We review the theory briefly with minimum repetition of material that has been given at length elsewhere [1–7].

In the internal variable formalism, the free energy density $(^1)\psi$ (per unit undeformed volume) of a continuous medium, is a function of the deformation, expressed in terms of the Right Cauchy-Green tensor $\mathbf{C}$, the temperature θ and N internal variables q_r, which, in general, may be components of tensor quantities $\mathbf{q}$; the latter are meant to transform as tensors with rotation of the material coordinate system but should remain invariant

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$(^1)$ Measured over and above its value at a reference equilibrium state.

with rotation of the spatial coordinate system in order that the principle of material indifference be satisfied.

The stress tensor τ and the entropy density η, per unit undeformed volume, are then found by differentiating ψ with respect to C and θ respectively, in accordance with the following equations:

(1.1)
$$\tau = \frac{2\varrho}{\varrho_0} \frac{\partial \psi}{\partial C},$$

(1.2)
$$\eta = -\frac{\partial \psi}{\partial \theta},$$

where ϱ and ϱ_0 are the current and reference mass densities respectively. In addition, the time rate of change of the entropy density of a specific material volume must satisfy the Clausius-Duhem inequality:

(1.3)
$$\dot{\eta} \geqslant -\frac{h^\alpha_{,\alpha}}{\theta},$$

where heat sources and sinks have been assumed absent and h^α is the heat flux vector per unit undeformed area.

It was shown in Ref. [1] that ineq. (1.3) follows from the postulate that the free energy of an infinitesimal material volume([2]), with a stationary boundary and under isothermal conditions, cannot increase. Conversely, ineq. (1.3) in conjunction with the first law of thermodynamics,

(1.4)
$$\dot{\varepsilon} = \frac{2\varrho}{\varrho_0} \tau^{\alpha\beta} \dot{C}_{\alpha\beta} - h^\alpha_{,\alpha}$$

yields the fundamental inequality

(1.5)
$$\dot{\psi}|_{C,\theta} \leqslant 0$$

whereupon one recovers the postulate from which ineq. (1.3) was derived. It follows, therefore, that in the internal variable formalism, ineq. (1.5) is an alternative statement of the Clausius-Duhem inequality. One may now introduce the irreversible entropy density γ such that

(1.6)
$$\dot{\eta} = -\frac{h^\alpha_{,\alpha}}{\theta} + \dot{\gamma}$$

whereupon the above inequality may be stated in terms of γ in the form:

(1.7)
$$\dot{\gamma} \geqslant 0.$$

It follows directly that

(1.8)
$$\theta\dot{\gamma} = -\dot{\psi}|_{C,\theta}$$

whereupon one deduces from Eqs. (1.6) and (1.8) the relation

(1.9)
$$-h^\alpha_{,\alpha} = -\theta\left(\frac{\partial \psi}{\partial \theta}\right)^{\cdot} + \frac{\partial \psi}{\partial q_r} \dot{q}_r$$

which is basic in the derivation of the heat conduction equation in dissipative media.

([2]) Henceforth called the microsystem.

The theory as it stands so far, applies to all irreversible systems. As a consequence, it cannot completely describe the thermomechanical behavior of any particular system, that being determined by the constitution of the system in question. For this to be achieved one must introduce a constitutive relation between the heat flux vector and the temperature gradient (the relation may also involve C, θ and q_r) as well as N *internal* constitutive equations which determine how the hitherto unknown functions q_r depend on time, given the deformation and temperature histories $C(t)$ and $\theta(t)$ respectively.

As far as the heat flux vector is concerned and using Fourier's law of heat conduction as a guide, one looks for a relation of the type:

$$(1.10) \qquad h^\alpha = h^\alpha(\theta, \alpha; C, \theta, q_r)$$

such that the heat flux vanishes when the temperature gradient becomes zero. Regarding the internal constitutive equations, these are arrived at by an argument that we have used in the past and we proceed to explain briefly below.

As a result of Eq. (1.8), $\dot\gamma$ must be some function g of C, θ, q_r, and $\dot q_r$, i.e.,

$$(1.11) \qquad \theta\dot\gamma = g(\dot q_r, q_r, C, \theta)$$

such that $g = 0$ when $\dot q_r = 0$. Furthermore, g cannot be linear in $\dot q_r$, otherwise ineq. (1.7) could be violated in the case of slow motions. Hence without loss of generality, we may write $\dot\gamma$ in the form

$$(1.12) \qquad \theta\dot\gamma = b_{rs}\dot q_r \dot q_s,$$

where the matrix b_{sr} is positive definite (by assumption[3] symmetric) and the coefficients b_{rs} may be functions of C, θ, q_r and $\dot q_r$. In particular for slow motions in which case $\dot\gamma$ is merely quadratic in $\dot q$, b_{rs} may depend only on C, θ and q_r. Equations (1.8) and (1.12) now yield

$$(1.13) \qquad \left(\frac{\partial\psi}{\partial q_r} + b_{rs}\dot q_r\right)\dot q_r = 0.$$

One observes that Eq. (1.13) will always be satisfied if (this being a sufficient condition)

$$(1.14) \qquad \frac{\partial\psi}{\partial q_r} + b_{rs}\dot q_r = 0$$

for all $r = 1, 2, \ldots, N$.

Equations (1.14) are the N additional *internal* constitutive equations which, now, render the thermomechanical response of a system completely determinate, if the functional form of ψ and the matrix b_{rs} are known.

2. The notion of internal inertia

In the treatment of polymeric materials as dissipative thermodynamic systems [7] we were able to identify the internal variables as *displacements* along the length of a typical macromolecule, interior to a microsystem. Evidently, a microsystem cannot be vanishingly

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[3] See, however, discussion in Sec. 4.

small if notions of average quantities, such as density and stress, for instance, are to retain their validity in a physical world which is patently discontinuous. Generalizing these remarks to pertain to other materials, then in so far as thermomechanical processes are concerned, the internal variables may be identified with displacements of material points, or statistical averages thereof (possibly tensorial), in the interior of a microsystem.

The deformation gradient field is of gross, or macroscopic character and pertains to a region R of gross dimensions. Superposed on this field exists an internal or microscopic displacement field which pertains to the constituent microsystems and is associated with the internal variables. Again with the macromolecule as a model, it was found that each particle experiences a force, henceforth referred to as an *internal* force, which was obtained by differentiating the free energy density with respect to the corresponding internal variable. We shall denote such a force by Q_r in which case in our notation[4],

$$(2.1) \qquad Q_r = \frac{\partial \psi}{\partial q_r}.$$

So long as the internal forces are not zero, the microsystem will not be in equilibrium and internal particles subject to these, will be in motion over and above their thermal motion. In the theoretical formalism as it stands today, this motion is opposed by a viscous resistance which for slow motions, at least, may be considered as a linear and homogeneous function of the particle velocities. In this event, and in accordance with Eq. (1.14)

$$(2.2) \qquad Q_r = -b_{rs}\dot{q}_s.$$

One may of course, encompass more general situations by allowing b_{rs} to depend on C, θ, q_r and $\dot{q}_r$, as discussed above.

It is evident that Eq. (2.2) does not take into account the inertia of the internal particles, henceforth called *internal inertia*, though the inertia of the microsystem as a whole has been accounted for in the macroscopic equation of motion. In particular, if we consider translational inertia this would be accounted for if Eq. (2.2) were made to read:

$$(2.3) \qquad Q_r = -b_{rs}\dot{q}_s - m_r\ddot{q}_r, \quad (r \text{ not summed}),$$

where m_r is the mass of the r'th particle. In this case one obtains the internal equation of motion,

$$(2.4) \qquad \frac{\partial \psi}{\partial q_r} + b_{rs}\dot{q}_s + m_r\ddot{q}_r = 0 \quad (r \text{ not summed}).$$

However Eq. (2.3) violates the Clausius-Duhem inequality as is indeed demonstrated in Appendix I. Yet Eq. (2.3) is a physically sound equation of internal motion. The situation certainly poses a paradox. The paradox is resolved by the realization that the internal motion of the microsystem now involves kinetic energy (above and beyond its thermal energy), which is convertible to internal potential energy, and hence is part of the free energy of the microsystem.

Thus when the internal inertia is accounted for, the free energy density must include the appropriate kinetic energy term, i.e.,

$$(2.5) \qquad \psi = \bar{\psi} + \frac{1}{2} \sum_r m_r\dot{q}_r^2,$$

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[4] In a more formal sense one may define such a force by Eq. (2.1).

where $\bar{\psi}$ is the "quasi-static" free energy which is a function of $\mathbf{C}$, θ, and q_r only. As a result, Eq. (2.4) may still be obtained if Q_r is given by the equation

$$(2.6) \qquad Q_r = \frac{\partial \psi}{\partial q_r} + \frac{d}{dt}\left(\frac{\partial \psi}{\partial \dot{q}_r}\right)$$

and Eq. (2.2) is retained. Now, as before

$$(2.7a) \qquad -Q_r \dot{q}_r = b_{sr} \dot{q}_r \dot{q}_s \geqslant 0$$

and furthermore,

$$(2.7b) \qquad \theta \dot{\gamma} = -\frac{d\psi}{dt}\bigg|_{\mathbf{C},\theta} = -\left[\frac{\partial \psi}{\partial q_r} + \frac{d}{dt}\left(\frac{\partial \psi}{\partial \dot{q}_r}\right)\right]\dot{q}_r = -Q_r \dot{q}_r \geqslant 0$$

i.e., the thermodynamic formalism presented in Sec. 1 survives intact *and the Clausius-Duhem inequality is not violated*, with the one notable exception that ψ now depends on $\dot{q}_r$ as well. With this new functional form for ψ, Eqs. (1.1) and (1.2) still hold, of course, as will be formally demonstrated in the following Section.

3. Existence of entropy in the presence of internal inertia

Recently, [1] we used the formalism of internal variables to show that in the case of dissipative systems, a thermodynamic entity known as *entropy* exists, and is a state function of $\mathbf{C}$, θ, and N internal variables q_r. The proof was based on a thermodynamic conjecture, that in the vicinity of a thermodynamic state of the microsystem (this being a point in the seven-dimensional state space of $\mathbf{C}$ and θ) there exist other states, which are not accessible from this point, by processes which are reversible and adiabatic. (The mathematical interpretation of a reversible process is one during which q_r remain constant.)

As pointed out previously the thermodynamic description of the system is made complete, by the introduction of N internal constitutive equations (given by Eq. (1.12) of the type:

$$(3.1) \qquad \dot{q}_r = f_r(q_s, \mathbf{C}, \theta).$$

We observe that(⁵)

$$(3.2) \qquad d\dot{q}_r = \frac{\partial f_r}{\partial q_s} dq_s + \frac{\partial f_r}{\partial \mathbf{C}} \cdot d\mathbf{C} + \frac{\partial f_r}{\partial \theta} d\theta.$$

Evidently processes for which $dq_r = 0$, $d\mathbf{C} \neq 0$, and $d\theta \neq 0$ are made possible by setting

$$(3.3) \qquad d\dot{q}_r = \frac{\partial f_r}{\partial \mathbf{C}} \cdot d\mathbf{C} + \frac{\partial f_r}{\partial \theta} d\theta.$$

When the internal inertia is accounted for, the internal constitutive equations are no longer given by Eq. (3.1) but by:

$$(3.4) \qquad \ddot{q}_r = f_r(q_s, \dot{q}_s, \mathbf{C}, \theta).$$

(⁵) The symbol d admits instantaneous infinitesimal changes of the quantity it precedes.

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The central property of this last equation is that it admits processes for which both dq_r and $d\dot{q}_r$ may vanish separately or jointly by suitably choosing the value of $d\ddot{q}_r$ in accordance with the relation

$$(3.5) \qquad d\ddot{q}_r = \frac{\partial f_r}{\partial q_s} dq_s + \frac{\partial f_r}{\partial \dot{q}_s} d\dot{q}_s + \frac{\partial f}{\partial \mathbf{C}} \cdot d\mathbf{C} + \frac{\partial f}{\partial \theta} d\theta.$$

Thus if both dq_r and $d\dot{q}_r$ vanish, then

$$(3.6) \qquad d\ddot{q}_r = \frac{\partial f}{\partial \mathbf{C}} \cdot d\mathbf{C} + \frac{\partial f}{\partial \theta} d\theta.$$

In other words q_r and $\dot{q}_r$ now play the role of independent variables. The proof of existence then follows directly, a reversible process being one during which *both* q_r and $\dot{q}_r$ remain constant.

In the terminology of Ref. [1] we assume that ε and τ are state functions of the state variables $\mathbf{C}$ and T (the Kelvin temperature) and $2n$ independent variables q_r and $\dot{q}_r$; in this event we write:

$$(3.7) \qquad \varepsilon = (\mathbf{C}, T, q_r, \dot{q}_r),$$

$$(3.8) \qquad \tau = \tau(\mathbf{C}, T, q_r, \dot{q}_r)$$

and we recall the first law (Eq. 1.4)

$$(3.9) \qquad \varepsilon = \frac{2\varrho}{\varrho_0} \tau^{\alpha\varrho} \dot{C}_{\alpha\beta} - h^\alpha, \alpha.$$

Following our theorem of Ref. [1] according to which the first law is integrable for processes which are reversible and adiabatic it follows that

$$(3.10) \qquad \frac{\partial \varepsilon}{\partial T} dT + \left(\frac{\partial \varepsilon}{\partial \mathbf{C}_{\alpha\beta}} - \frac{2\varrho}{\varrho_0} \tau_{\alpha\beta} \right) d\mathbf{C}_{\alpha\beta} = \theta d\eta \big|_{q_r, \dot{q}_r},$$

where

$$(3.11) \qquad \theta = \theta(\mathbf{C}, T, q_r, \dot{q}_r),$$

$$(3.12) \qquad \eta = \eta(\mathbf{C}, T, q_r, \dot{q}_r).$$

It follows from Eq. (3.11) that,

$$(3.13) \qquad \frac{\partial \varepsilon}{\partial T} \bigg|_{\mathbf{C}, q_r, \dot{q}_r} = \theta \frac{\partial \eta}{\partial T} \bigg|_{\mathbf{C}, q_r, \dot{q}_r},$$

$$(3.14) \qquad \frac{\partial \varepsilon}{\partial \mathbf{C}_{\alpha\beta}} \bigg|_{T, q_r, \dot{q}_r} - \frac{2\varrho}{\varrho_0} \tau^{\alpha\varrho} = \theta \frac{\partial \eta}{\partial \mathbf{C}_{\alpha\gamma}} \bigg|_{T, q_r, \dot{q}_r}.$$

If we now use θ as an independent variable and in addition we introduce the free energy density ψ, where

$$(3.15) \qquad \psi = \varepsilon - \eta\theta,$$

$$(3.16) \qquad \psi = \psi(\mathbf{C}, \theta, q_r, \dot{q}_r),$$

one obtains equations analogous to (1.1) and (1.2) i.e.,

$$(3.17) \qquad \tau^{\alpha\beta} = \frac{2\varrho}{\varrho_0} \left. \frac{\partial \psi}{\partial C_{\alpha\beta}} \right|_{\theta, q_r, \dot{q}_r},$$

$$(3.18) \qquad \eta = -\left. \frac{\partial \psi}{\partial \theta} \right|_{C, q_r, \dot{q}_r}.$$

Furthermore, the postulate that ψ cannot increase under isothermal conditions when the boundary of the microsystem remains fixed i.e.,

$$(3.19) \qquad \dot{\psi}|_{C, \theta} \leqslant 0$$

or,

$$(3.20) \qquad \frac{\partial \psi}{\partial q_r} \dot{q}_r + \frac{\partial \psi}{\partial \dot{q}_r} \ddot{q}_r \leqslant 0,$$

in conjunction with the first law again leads to the Clausius-Duhem inequality

$$(3.21) \qquad \dot{\eta} \geqslant -\frac{h^\alpha_{,\alpha}}{\theta}.$$

Or, if

$$(3.22) \qquad \dot{\eta} = \dot{\gamma} - \frac{h^\alpha_{,\alpha}}{\theta},$$

to the equivalent statement:

$$(3.23) \qquad \theta\dot{\gamma} = -\dot{\psi}|_{C, \theta} \geqslant 0.$$

Also the equation which related the divergence of the heat flux to the free energy, now reads

$$(3.24) \qquad -h^\alpha_{,\alpha} = -\theta\left(\frac{\partial \psi}{\partial \theta}\right)^{\boldsymbol\cdot} + \frac{\partial \psi}{\partial q_r} \dot{q}_r + \frac{\partial \psi}{\partial \dot{q}_r} \ddot{q}_r.$$

Finally the constitutive description of the microsystem is made complete by the internal constitutive equations

$$(3.25) \qquad Q_r = -b_{rs}\dot{q}_s,$$

where

$$(3.26) \qquad Q_r = \frac{\partial \psi}{\partial q_r} + \frac{d}{dt}\left(\frac{\partial \psi}{\partial \dot{q}_r}\right),$$

in accordance with our discussion in Sec. 2.

4. Lagrangian density and total dissipation

In this section we introduce a new thermodynamic density which we shall call the *Lagrangian density* and thereby derive a functional of the Lagrangian density which has the physical significance of a temperature-averaged total dissipation, henceforth referred to as *total dissipation*.

As a first step is worth discussing([6]) Eq. (3.25). To make the discussion specific and to keep this article to a reasonable length, we shall assume that $\vec{Q}_r$ and $\vec{q}_r$ are absolute vectors (as indicated) and, therefore change sign with reflection of the reference coordinate frame (in this case the material reference frame). We shall further assume that we are dealing with a medium whose properties remain unchanged with reflection of the material reference frame. Now since the matrix b_{rs} is merely transposed upon reflection, then to satisfy constitutive invariance with respect to this operation we must have as necessary and sufficient condition that([7])

$$(4.1) \qquad b_{rs}(\mathbf{C}, \theta, \vec{q}_r) = b_{sr}(\mathbf{C}, \theta, -\vec{q}_r),$$

since $\mathbf{C}$ and θ remain unchanged upon reflection. In particular, if b_{rs} does not depend on $\vec{q}_r$ then

$$(4.2) \qquad b_{rs} = b_{sr}.$$

These are, of course, the Onsager relations. If on the other hand q_r are scalars, which of course do not change sign with reflection of the coordinate system, then always

$$(4.3) \qquad b_{rs}(\mathbf{C}, \theta, q_r) = b_{sr}(\mathbf{C}, \theta, q_r).$$

The physical grounds on which one would argue whether ot not b_{rs} is a diagonal matrix are now fairly clear. It follows from Eq. (3.25) that b_{rs} is the magnitude of the force that particle r would experience as a result of the motion of particle s having a velocity of unit norm with all other particles stationary. If therefore we exclude viscous action at a distance, as well as viscous interaction between nearest neighbors, then b_{rs} will become a diagonal matrix. One would expect that such an ideal state of affairs will be approched asymptotically as the velocity of the particles becomes vanishingly small. On the other hand it has been shown elsewhere that in the case of linear systems, one may introduce generalized variables q_r with respect to which b_{rs} is diagonal even though viscous action at a distance is not zero.

In the present paper we shall assume that b_{rs} is diagonal in which case the relation between the internal force Q_r and the particle velocity $\dot{q}_r$ is of the form:

$$(4.4) \qquad Q_r = -\dot{q}_r \zeta_r \qquad r \text{ not summed}([8]).$$

In view of previous discussion and as a result of Eqs. (4.4) and (4.5) it follows that

$$(4.5) \qquad Q_r = -b_r\left(\frac{\partial \psi}{\partial \dot{q}_r}\right) \qquad r \text{ not summed},$$

where

$$(4.6) \qquad b_r = \left(\frac{\zeta_r}{m_r}\right).$$

([6]) A more complete discussion of this equation will appear in a forthcoming paper.

([7]) In this paper we shall limit this discussion to cases where b_{rs} does not depend on $\dot{q}_r$.

([8]) The functions ζ_r are understood to depend on $\mathbf{C}$ and θ. This dependence will not be shown explicitly. Also, ζ_r will henceforth be independent of q_r and $\dot{q}_r$.

Thus as a result of Eqs. (3.26) and (4.5) the N internal constitutive equations are now expressible solely in terms of ψ, i.e.,

$$(4.7) \qquad \frac{d}{dt}\left(\frac{\partial \psi}{\partial \dot{q}_r}\right)+b_r\frac{\partial \psi}{\partial \dot{q}_r}+\frac{\partial \psi}{\partial q_r}=0 \quad r \text{ not summed.}$$

The Lagrangian density function

At the point we introduce a thermodynamic density V, which has not hitherto been encountered in thermodynamics. The function V bears resemblance to the Lagrangian L of classical mechanics and is defined as

$$(4.8) \qquad V = \sum_r 1/2m_r\dot{q}_r^2 - \psi$$

and is, in fact, the difference between the "internal velocity" potential and the free energy density.

We note the following relations:

$$(4.9), (4.10) \qquad \frac{\partial V}{\partial q_r} = -\frac{\partial \psi}{\partial q_r}, \qquad \frac{\partial V}{\partial \dot{q}_r} = \frac{\partial \psi}{\partial \dot{q}_r}.$$

The following, also important, relation results from Eq. (4.5):

$$(4.11) \qquad Q_r = -b_r\frac{\partial V}{\partial \dot{q}_r}, \qquad r \text{ not summed.}$$

The force Q_r may now be expressed in terms of the Lagrangian density by the relation

$$(4.12) \qquad Q_r = \frac{d}{dt}\left(\frac{\partial V}{\partial \dot{q}_r}\right) - \frac{\partial V}{\partial q_r}, \qquad r \text{ not summed}$$

which in conjunction with Eqs. (4.5) and (4.9) yields the N internal constitutive equations totally in terms of the Lagrangian density V:

$$(4.13) \qquad \frac{d}{dt}\left(\frac{\partial V}{\partial q_r}\right)+b_r\frac{\partial V}{\partial \dot{q}_r}-\frac{\partial V}{\partial q_r}=0, \qquad r \text{ not summed.}$$

In the remainder of this work we shall be concerned exclusively with systems which we shall call "energetically additive", in the sense that their free energy may be expressed in the additive form,

$$(4.14) \qquad \psi = \psi_0(\mathbf{C},\theta)+\sum_r\left[\bar{\psi}_r(\mathbf{C},\theta,q_r)+\frac{1}{2}m_r\dot{q}_r^2\right],$$

where $\bar{\psi}_r$ is a function of $\mathbf{C}$, θ and q_r only. Such systems form a large class, of which linear systems are a small sub-class. As a result of our additivity hypothesis

$$(4.15) \qquad V = V_0(\mathbf{C},\theta)+\sum_r V_r,$$

where V_r is a function of $\mathbf{C}$, θ, q_r and $\dot{q}_r$ only.

To derive our principle of *stationary total dissipation* we begin with the following relations which are necessary for our purposes:

$$(4.16) \qquad \overset{*}{V_r} \equiv \left.\frac{dV}{d\tau}\right|_{C,\,\theta} = \frac{\partial V}{\partial q_r}\dot{q}_r + \frac{\partial V}{\partial \dot{q}_r}\ddot{q}_r$$

or,

$$(4.17) \qquad \overset{*}{V_r} = \frac{d}{d\tau}\left(\frac{\partial V_r}{\partial \dot{q}_r}\right) - Q_r\dot{q}_r, \qquad r \text{ not summed,}$$

where we have used Eq. (4.11). Furthermore, use of Eq. (4.11) in Eq. (4.17) yields,

$$(4.18) \qquad \overset{*}{V_r} = -\frac{d}{d\tau}\left(\frac{Q_r\dot{q}_r}{b_r}\right) - \left(\frac{Q_r\dot{q}_r}{b_r}\right)b_r, \qquad r \text{ not summed.}$$

This last equation may now be integrated to give,

$$(4.19) \qquad Q_r\frac{dq_r}{d\xi_r} = -\int_0^{\xi_r} e^{-(\xi_r-\xi')}\left.\frac{\partial V_r}{\partial \xi'}\right|_{C,\,\theta} d\xi' \qquad r \text{ not summed,}$$

where

$$(4.20) \qquad \xi_r = \int_0^t b_r(\tau)\,d\tau.$$

The time rate of change of the irreversible entropy, $\dot{\gamma}$, may now be obtained readily from Eqs. (2.7) and (4.19) and in fact:

$$(4.21) \qquad \theta\dot{\gamma} = \sum b_r \int_0^{\xi_r} e^{-(\xi_r-\xi_r')}\left.\frac{\partial V_r}{\partial \xi'}\right|_{C,\,\theta} d\xi'.$$

At this point, we introduce the temperature-averaged total irreversible entropy Γ, where

$$(4.22) \qquad \Gamma = \int_0^t \theta\frac{d\gamma}{d\tau}\,d\tau$$

and call this quantity Total Dissipation Density, or, *total dissipation*, for short. Equation (4.20) may then be integrated to yield the following expression for the Total Dissipation:

$$(4.23) \qquad \Gamma = \sum_r \int_0^{\xi_r} e^{-(\xi_r-\xi_r')}\,\Delta V_r(\xi')\,d\xi',$$

where $\Delta V_r = V_r(C, \theta, q_r, \dot{q}_r) - V_r(C, \theta, 0, 0)$.

Evidently the Total Dissipation is a functional of the Lagrangian Density.

(*) Where conflict is not likely to arise, a dot over a quantity may denote differentiation with respect to t or τ.

5. Principle of stationary total dissipation

We now proceed to establish a variational principle, totally new in the field of irreversible thermodynamics, which is akin to Hamilton's Principle of classical mechanics. This principle is yet another manifestation of the latent analogies that exist between irreversible thermodynamics and classical mechanics.

Consider a system which at $t = 0$ is in a state of equilibrium. We may assume without loss of generality that in this state $q_r = \dot{q}_r = 0$. At time $t = 0$, the system is subject to a thermomechanical disturbance which is described by the deformation and temperature histories $C(t)$ and $\theta(t)$, respectively. Then as a result of Eq. (4.14) and the initial conditions, the history of the internal variables $q_r(t)$ may be determined. Let us define an Internal State Space, or a q-space, as an N-dimensional Euclidian space with coordinates $q_1, q_2, \ldots, q_N$. The internal state of the system which is given by the n-tuple of numbers $(q_1, q_2, \ldots, q_N)$, is represented by a point in q-space.

When the equilibrium of the system is disturbed, as a result of the thermomechanical history $C(t)$ and $\theta(t)$, the internal state of the system will change and its evolution with time will be given by a curve, or trajectory, in q-space, this trajectory being determined by Eq. (4.14). We are now in a position to propose the Principle of Stationary Total Dissipation in the form of the following theorem, for energetically additive systems.

THEOREM. *Given a thermomechanical history $C(t)$ and $\theta(t)$, the total dissipation functional $\Gamma(t)$ has a stationary value for the actual trajectory in q-space, as opposed to adjacent trajectories that emanate from the origin at time $t = 0$ and terminate at the terminal point of the actual path at time t.*

Let ORP be the actual trajectory in q-space (O and P being the endpoints of the trajectory and R an intermediate point) described by the functions $q_r(\tau)$ ($r = 1, 2, \ldots, N$), $0 \leqslant \tau \leqslant t$, and suppose that the functions $\bar{q}_r(\tau)$ describe another trajectory $OR'P$ with the same endpoints as the actual trajectory, R' being an intermediate point of the new trajectory. It is said that the trajectory ORP is in the neighborhood h of $OR'P$ if

$$(5.1) \qquad \left\{ \sum_r \int_0^t [\bar{q}_r(\tau) - q_r(\tau)] [\bar{q}_r(\tau) - q_r(\tau)] d\tau \right\}^{1/2} < h,$$

where h is a vanishingly small number. To ensure that $OR'P$ is in the neighborhood h of ORP we introduce functions $\eta_r(\tau)$, continuous and twice differentiable and a small positive number ε such that

$$(5.2) \qquad \bar{q}_r(\tau) = q_r(\tau) + \varepsilon \eta_r(\tau).$$

Let

$$(5.3) \qquad k^2 = \left| \sum_r \int_0^t \eta_r(\tau)\eta_r(\tau) d\tau \right|_{\text{sup}}.$$

Then ORP will be in the neighborhood h of $OR'P$ if

$$(5.4) \qquad \varepsilon < \frac{h}{k}.$$

One can always choose ε sufficiently small to satisfy the above condition.

Let

(5.5) $\delta \Gamma = \Gamma(OR'P) - \Gamma(ORP)$

in obvious notation. Then to a first order in ε,

(5.6) $\Gamma + \delta \Gamma = \sum_{r=1}^{N} \int_{0}^{\xi_r} e^{-(\xi_r - \xi_r')} \Delta V_r(q_r + \varepsilon \eta_r, \dot{q}_r + \varepsilon \eta_r) d\xi_r',$

where dependence of V on $\mathbf{C}$ and θ has been suppressed (since the latter two are fixed and a variation on these is not called for) and

(5.7) $\xi_r = \int_{0}^{t} b_r d\tau.$

Assuming that V_r is sufficiently smooth to be represented by its Taylor expansion in the vicinity of q_r and $\dot{q}_r$ and retaining only terms of order ε, then Eq. (5.6) reduces to:

(5.8) $\Gamma + \delta \Gamma = \sum_{r=1}^{N} \int_{0}^{\xi_r} e^{-(\xi_r - \xi_r')} \Delta V_r d\xi_r' + \varepsilon \sum_{r=1}^{N} \int_{0}^{\xi_r} e^{-(\xi_r - \xi_r')} V_{r\delta} d\xi',$

where

(5.9) $V_{r\delta} \equiv \frac{\partial V_r}{\partial q_r} \eta_r + \frac{\partial V_r}{\partial \dot{q}_r} \dot{\eta}_r,$ r not summed.

Thus

(5.10) $\delta \Gamma = \varepsilon \sum_{r=1}^{N} \int_{0}^{\xi_r} e^{-(\xi_r - \xi_r')} \left[\frac{\partial V_r}{\partial q_r} \eta_r + \frac{\partial V_r}{\partial \dot{q}_r} \dot{\eta}_r \right] d\xi_r',$

where a dot over a quantity denotes differentiation with respect to τ. If now one integrates by parts the second term in the bracket under the integral sign, Eq. (5.10) reduces to:

(5.11) $\delta \Gamma = \varepsilon \sum_{r=1}^{N} e^{-\xi_r} \int_{0}^{\xi_r} \left\{ \frac{\partial V_r}{\partial q_r} - \frac{d}{d\tau} \left[e^{\xi_r} \frac{\partial V_r}{\partial \dot{q}_r} \right] \right\} \eta_r d\xi_r'$

on account of the fact that $\eta_r(0) = \eta_r(\xi_r) = 0$. It follows readily that

(5.12) $\delta \Gamma = \varepsilon \sum_{r=1}^{N} \int_{0}^{\xi_r} e^{-(\xi_r - \xi_r')} \left\{ \frac{\partial V_r}{\partial q_r} - b_r \frac{\partial V_r}{\partial \dot{q}_r} - \frac{d}{d\tau} \left(\frac{\partial V_r}{\partial \dot{q}_r} \right) \right\} \eta_r d\xi_r'.$

However, the bracket under the integral and therefore the integral itself vanishes as a result of the internal constitutive Eqs. (4.14). Hence:

(5.13) $\delta \Gamma = 0,$

i.e. Γ is stationary with respect to trajectories in a vanishingly small neighborhood h of the actual trajectory ORP, and the theorem is proved.

The following Lemma follows easily and we give it without proof:

LEMMA. *A trajectory OP in q-space [given $C(\tau)$ and $\theta(\tau)$] is an actual trajectory if it renders the total dissipation Γ stationary with respect to other trajectories in the neighborhood of OP.*

Postscript

In two recent papers [8, 9] on viscoplastic materials we showed that Eqs. (1.14) also hold in the case where the time scale, with respect to which the rate of q_s is calculated, is an *intrinsic* time scale which does not necessarily coincide with the time scale of an ordinary clock. The present theory applies, strictly, to viscoelastic materials. However, the possibility of applying the theory to materials which are viscoplastic, in the above sense, should be evident to the reader.

Appendix I

The purpose of the Appendix is to illustrate a case where the Clausius-Duhem inequality is violated when the internal inertia force is included in the equation of internal motion but the free energy density remains a function of C, θ and q_r, only.

Consider a linear material with one internal variable and in a uniaxial isothermal state of stress. In this event

(A.1)
$$\psi = \frac{1}{2}A\varepsilon^2 - B\varepsilon q + \frac{1}{2}Cq^2,$$

where A, B and C are constants. If the internal inertia is accounted for, the internal constitutive equation becomes:

(A.2)
$$\frac{\partial \psi}{\partial q} + \eta\dot{q} + m\ddot{q} = 0$$

or, as a result of Eq. (1.1):

(A.3)
$$Cq + \eta\dot{q} + m\ddot{q} = B\varepsilon,$$

where C, η and m are all positive constants.

Let the material undergo a motion which consists of "uniaxial oscillation" at the resonant frequency $\omega = \sqrt{C/m}$, i.e., let

(A.4)
$$\varepsilon = \varepsilon_0 \sin\sqrt{\frac{C}{m}}t.$$

Then it transpires that

(A.5)
$$q = q_0 \cos\sqrt{\frac{C}{m}}t,$$

where

(A.6)
$$q_0 = -\frac{B\varepsilon_0}{\eta}\sqrt{\frac{m}{C}}.$$

It follows that

(A.7)
$$\theta_0 \dot{\gamma} = -\frac{\partial \psi}{\partial q} \dot{q} = \frac{B^2 \varepsilon_0^2}{2\eta} \left\{ 1 - \cos 2\omega t + \frac{m\omega}{\eta} \sin 2\omega t \right\},$$

where θ_0 is the (constant) reference temperature.

A sufficient condition that $\dot{\gamma}$ will become negative is that

(A.8)
$$m > \frac{\eta^2}{C}$$

in which case $\theta_0 \dot{\gamma}$ will attain a maximum *negative* value of

$$\frac{B^2 \varepsilon_0^2}{2\eta} \left\{ 1 - \frac{m\omega}{\eta} \right\}.$$

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