Proper tensorial formulation of the internal variable theory
The endochronic time spectrum

K. C. VALANIS (IOWA CITY)

IN THE COURSE of the development of the theory of irreversible thermodynamics of internal variables, scant attention has been given to the precise tensorial character of the internal variables. Specifically their transformation properties in rotating spatial and/or material reference frames have not been investigated to any major extent. In this paper we admit internal variables which transform as tensors with rotation of the spatial system of coordinates thus obtaining a spatial formulation of thermodynamics of internal variables; in the event that these are tensors in the material coordinate system, care is taken to distinguish between the covariant, contravariant and mixed components. This distinction gives rise to different constitutive equations depending on which components are chosen as independent variables. Finally the intrinsic time spectrum is introduced with some interesting consequences.

W procesie rozwoju teorii termodynamiki procesów nieodwracalnych, operującej pojęciem zmiennych wewnętrznych, niewiele uwagi zwracano na precyzyjne sformułowanie tensorowego charakteru zmiennych wewnętrznych. W szczególności, nie zbadano zbyt dokładnie ich własności transformacyjnych względem obracających się, materialnych oraz/lub przestrzennych układów odniesienia. W niniejszej pracy dopuszcza się istnienie zmiennych wewnętrznych, które transformują się jak tensory przy obrocie przestrzennych układów współrzędnych, co prowadzi do przestrzennego sformułowania termodynamiki zmiennych wewnętrznych; w przypadku, gdy są one tensorami w materialnych układach odniesienia, zwraca się uwagę na rozróżnienie ich składowych kowariantnych, kontrawariantnych i mieszanych. Rozróżnienie to prowadzi do różnych równań konstytutywnych, w zależności od tego, które składowe wybierzemy jako zmienne niezależne. Na koniec wprowadza się pojęcie wewnętrznego widma czasowego prowadzącego do pewnych interesujących wniosków.

В процессе развития теории термодинамики необратимых процессов, оперирующей понятием внутренних переменных, немного внимания обращено на точную формулировку тензорного характера внутренних переменных. В частности не исследованы слишком точно их трансформационные свойства по отношению к вращающимся, материальным или пространственным системам отсчета. В настоящей работе допускается существование внутренних переменных, которые преобразуются как тензоры при вращении пространственных систем координат, что приводит к пространственной формулировке термодинамики внутренних переменных; в случае, когда они являются тензорами в материальных системах отсчета, обращается внимание на различимость их ковариантных, контравариантных и смешанных составляющих. Эта различимость приводит к разным определяющим уравнениям в зависимости от того, которые составляющие избраны как независимые переменные. Наконец вводится понятие внутреннего временного спектра, приводящего к некоторым интересным следствиям.

Introduction

IN THE INTERNAL variable formalism of irreversible thermodynamics, the free energy density ψ of a continuous medium is a function of the deformation gradient $\frac{\partial y_i}{\partial x^\alpha}$ (henceforth denoted by $y_{i\alpha}$), the temperature θ and N internal variables $\mathbf{q}_r$. The latter are such that their current values, as well as those of $y_{i\alpha}$ and θ, are necessary and sufficient for the de-

termination of the thermodynamic state of an infinitesimal element of a material con-figuration.[*]

Though generally recognized [2–10] that q_r may be scalars, vectors or tensors, very scant attention has been given to the consequences of the precise tensorial nature of q_r. On occasion, explicit constitutive equations, that apply to large deformation, have been derived using *proper tensor formulation* [11] but these occasions have been rare. In Ref. [11], q_r were regarded as quantities which transform as tensors with rotation of the material system of coordinates x^α, but remain invariant with rotation of the spatial system. This was also done in Ref. [12], where constitutive equations which apply to viscoplastic materials were derived, under conditions of large deformation.

In this paper we examine in detail the consequences of the precise tensorial nature of the internal variables. In the first place, we admit internal variables which transform as tensors with rotation of the *spatial system* of coordinates, thus giving rise to a *spatial formulation* of the thermodynamics of internal variables.

In the event that q_r are tensors in the material coordinate system, care has been taken to distinguish between their covariant, contravariant and mixed components, a subtle point that has not been given due attention hitherto. Such distinction gives rise to different constitutive equations depending on which components have been chosen as independent variables.

Pursuing an analysis along this avenue we have shown that constitutive equations may be derived which contain no reference to the original material configuration. Such constitutive equations, of course, apply to simple fluids in the sense of COLEMAN [13]. Again we are not aware of a previous derivation of constitutive fluid equations, using the formalism of internal variables.

In the latter parts of the paper we generalize the concept of intrinsic time, by introducing the concept of a spectrum of intrinsic times. Such a generalization follows naturally by assigning to each internal variable a characteristic intrinsic time scale, so that the resulting equations apply readily to a material whose equilibrium response is "plastic" (i.e., history dependent but rate independent) but whose transient response is rate dependent. Such materials are viscoplastic in the accepted sense (MALVERN [14], PERZYNA [15], PERZYNA and WOJNO [9]).

PERZYNA and WOJNO [9] dealt with such materials by using the internal variable theory to describe their transient response, but classical plasticity to describe their equilibrium response.

2. Viscoelastic solids

2.1. Spatial and material characterization

Let the free energy density ψ be a function of the deformation gradient $y_{i\alpha}$ the temper-ature θ and n internal variables $q_{ij}^{(r)}$, independent of $y_{i\alpha}$. The internal variables are specified to be symmetric second order tensors in the spatial frame y_i. In other words, the com-ponents $\bar{q}_{ij}^{(r)}$ in a spatial frame $\bar{y}_i$, such that

$$(2.1) \qquad\qquad\qquad \bar{y}_i = Q_{ij}y_i,$$

[*] For a more precise definition of this statement see Ref. [1].

where Q_{ij} is a proper orthonormal matrix, are given by the transformation

(2.2) $$\bar{q}_{ij}^{(r)} = Q_{ik}Q_{jl}q_{kl}^{(r)}.$$

The following equations are a direct consequence of the internal variable theory [5, 6]:

$$T_i^\alpha = \frac{\varrho}{\varrho_0}\frac{\partial\psi}{\partial y_{i\alpha}},$$

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

$$\frac{\partial\psi}{\partial q_{kl}^{(r)}}\dot{q}_{kl}^{(r)}\Big|_{y_{i\alpha}} \leqslant 0,$$

where

(2.4) $$\psi = \psi(y_{i\alpha}, \theta, q_{ij}^{(r)}).$$

The spatial components T_{ij} of the stress tensor may be obtained from Eq. (2.3)$_1$ by the transformation

(2.5) $$T_{ij} = \frac{1}{2}\frac{\varrho}{\varrho_0}\left(\frac{\partial\psi}{\partial y_{i\alpha}}y_{j\alpha} + \frac{\partial\psi}{\partial y_{j\alpha}}y_{i\alpha}\right).$$

The stress components $\tau^{\alpha\beta}$ in the material system, are related to T_{ij} by the transformation

(2.6) $$\tau^{\alpha\beta} = x_i^\alpha x_j^\beta T_{ij},$$

where $x_i^\alpha = \dfrac{\partial x^\alpha}{\partial y_i}$. In the particular case where the material is incompressible then the relation (2.3)$_1$ must be replaced by the equation

(2.7) $$T_i^\alpha = \frac{\partial\psi}{\partial y_{i\alpha}} - px_i^\alpha$$

where p is an arbitrary hydrostatic pressure.

It has been shown previously [16] that if the material is isotropic then ψ must depend on $y_{i\alpha}$ through the left Cauchy-Green tensor B_{ij} where

(2.8) $$B_{ij} = y_{i\alpha}y_{j\alpha}.$$

Thus the functional dependence of ψ on the deformation will, in this case, be of the form

(2.9) $$\psi = \psi(B_{ij}, \theta, q_{ij}^{(r)}).$$

It is also essential that the functional form of ψ meets the condition of material indifference. This is accomplished by requiring that ψ depends only on the joint invariants of δ_{ij}, B_{ij}, and $q_{ij}^{(r)}$ where δ_{ij} is the unit matrix.

Following our previous work we introduce n internal constitutive equations — i.e., equations of evolution of the internal variables, in the form[*]

2.10) $$\frac{\partial\psi}{\partial q_{ij}^{(r)}} + b_{ijkl}\hat{q}_{kl}^{(r)} = 0,$$

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[*] For a scalar treatment of the internal variables see [3, 6 and 17].

where $b_{ijkl}^{(r)}$ is a material viscocity tensor — in this case isotropic — and $\hat{q}_{kl}$ is one of a class of objective derivatives of $q_{kl}^{(r)}$, with the property:

$$(2.11) \qquad\qquad \hat{q}_{kl}^{(r)}\big|_{y_{i\alpha}} = \dot{q}_{kl}^{(r)}\big|_{y_{i\alpha}}.$$

In other words, the objective derivative of $\mathbf{q}^{(r)}$ and the material derivative of $\mathbf{q}^{(r)}$ with $y_{i\alpha}$ remaining constant, are identical. In view of Eq. (2.11), it follows that Eq. (2.10) will satisfy the inequality (2.3)$_3$ provided that b_{ijkl} is a positive semi-definite fourth order tensor.

It is our purpose, in this section, to show that different choices of objective derivatives of $\mathbf{q}^{(r)}$ give rise to different constitutive equations, even though the form of ψ remains the same. We shall further find that this formulation leads to constitutive equations with specific characteristics that make them inapplicable to a class of materials commonly referred to as "fluids". This point will be discussed at length at the end of this section.

ψ — *forms quadratic in* $\mathbf{q}^{(r)}$

For the purpose of discussion we shall focus our attention on a class of incompressible materials where ψ is a quadratic function of the internal variables, i.e.,

$$(2.12) \qquad\qquad \psi = \psi_0(\mathbf{B}) + A^{(r)}B_{ij}q_{ij}^{(r)} + \frac{1}{2}C^{(r)}q_{ij}^{(r)}q_{ij}^{(r)}$$

and $b_{ijkl}^{(r)}$ is of the form:

$$(2.13) \qquad\qquad b_{ijkl}^{(r)} = b^{(r)}\delta_{ik}\delta_{jl}.$$

As a result of Eqs. (2.5), (2.7) and (2.12),

$$(2.14) \qquad\qquad T_{ij}+p\delta_{ij} = 2B_{ik}\frac{\partial\psi_0}{\partial B_{kj}} + (q_{il}^{(r)}B_{jl}+q_{jl}^{(r)}B_{il})A^{(r)},$$

whereas use of equations (2.10), (2.12) and (2.13) yields a set of r internal constitutive equations in $\mathbf{q}^{(r)}$ of the form

$$(2.15) \qquad\qquad C^{(r)}\mathbf{q}^{(r)}+b^{(r)}\hat{\mathbf{q}}^{(r)}+A^{(r)}B = 0 \qquad (r \text{ not summed}).$$

These are linear first order differential equations in the q's, which can be integrated analytically. Substitution of $\mathbf{q}^{(r)}$ in Eq. (2.14) will then yield the appropriate constitutive equation which relates the stress to the deformation history of the material at hand. This we shall proceed to do with various choices of the objective derivatives $\hat{\mathbf{q}}^{(r)}$ of $\mathbf{q}^{(r)}$.

2.2. Cases of objective derivatives

$$(2.16)_1 \qquad\qquad \hat{q}_{ij}^{(r)} = \dot{q}_{ij}^{(r)}+q_{ik}v_{k,j}+q_{kj}v_{k,i}.$$

We observe the following identity:

$$(2.16)_2 \qquad\qquad \hat{q}_{ij}^{(r)} = x_i^\alpha x_j^\beta \dot{q}_{\alpha\beta}^{(r)},$$

where $q_{\alpha\beta}^{(r)}$ are the covariant components of $\mathbf{q}_{\mathbf{c}}^{(r)}$, i.e.,

$$(2.17) \qquad\qquad q_{\alpha\beta}^{(r)} = y_{i\alpha}y_{j\beta}q_{ij}^{(r)}.$$

Equations (2.15)–(2.17) combine to yield the first order differential equation

(2.18)
$$C^{(r)}q_{\alpha\beta}^{(r)} + b^{(r)}\dot{q}_{\alpha\beta}^{(r)} + A^{(r)}C_{\alpha\mu}C_{\mu\beta} = 0,$$

where $C_{\alpha\beta}$ is the right Cauchy-Green tensor given by the relation

(2.19)
$$C_{\alpha\beta} = y_{i\alpha}y_{i\beta}.$$

Equation (2.18) is solved in conjunction with the initial condition that at $t = -\infty$ the material is in an undisturbed equilibrium in which the stress field is at most hydrostatic. In this event

$$\mathbf{q}_r|_{t=-\infty} = 0, \ \mathbf{B}|_{t=-\infty} = \mathbf{C}|_{t=-\infty} = \boldsymbol{\delta}.$$

The solution of equation (2.18) then is:

(2.20)
$$\mathbf{q}^{(r)} = -\frac{A^{(r)}}{b^{(r)}} \int_{-\infty}^{t} e^{-a_r(t-\tau)}\mathbf{C}^2(\tau)d\tau,$$

where

$$a_r = \frac{C^{(r)}}{b^{(r)}}.$$

The resulting constitutive equation is the following:

(2.21)
$$\mathbf{T} + \mathbf{p} = 2\mathbf{B}\frac{\partial\psi}{\partial\mathbf{B}} - \int_{-\infty}^{t} G(t-\tau)\{\mathbf{c}(\tau)^{-1}\mathbf{B}(t)\mathbf{c}(\tau)^{-1}\mathbf{B}(t) + \mathbf{B}(t)\mathbf{c}(\tau)^{-1}\mathbf{B}(t)\mathbf{c}(\tau)^{-1}\}d\tau,$$

where

(2.22)
$$G(t) = \sum_r \frac{A^{(r)}}{b^{(r)}} e^{-a_r t},$$

and $\mathbf{c}^{-1}$ is the inverse of the relative Finger tensor $\mathbf{c}$ which is defined by the relation

(2.23)
$$c_{ij} = \frac{\partial y_i(t)}{\partial y_k(\tau)} \frac{\partial y_j(t)}{\partial y_k(\tau)}.$$

The representation of the constitutive Eq. (2.21) in the material system is given in the form of Eq. (2.14):

(2.24)
$$\tilde{\tau} + p\tilde{C} = 2\frac{\partial\psi}{\partial\mathbf{C}} - \int_{-\infty}^{t} \{\tilde{C}(t)\mathbf{C}^2(\tau) + \mathbf{C}^2(\tau)\tilde{C}(t)\}G(t-\tau)d\tau$$

where the components of $\tilde{\tau}$ are $\tau^{\alpha\beta}$, the components of $\tilde{C}$ are $C^{\alpha\beta}$ and $\tilde{C}C = \boldsymbol{\delta}$.

Other choices of the objective derivative of $\mathbf{q}^{(r)}$ are possible

(2.25)
$$\hat{q}_{ij}^{(r)} = \dot{q}_{ij}^{(r)} - q_{ik}^{(r)}v_{j,k} + q_{kj}^{(r)}v_{k,i}.$$

This derivative has the material representation

(2.26)
$$\hat{q}_{ij}^{(r)} = \dot{q}_\alpha^{(r)\beta}x_i^\alpha y_{j\beta}.$$

Here $q_\alpha^{(r)\beta}$ are the right mixed components of $\mathbf{q}^{(r)}$:

(2.27)
$$q_\alpha^{(r)\beta} = q_{ij}^{(r)}y_{i\alpha}x_j^\beta.$$

Use of Eqs. (2.10), (2.12), (2.25), and (2.26) yields a set of r internal constitutive equations in the form:

$$(2.28) \qquad C_\alpha^{(r)} q_\alpha^{(r)\beta} + b^{(r)} \dot{q}_\alpha^{(r)\beta} + A^{(r)} C_{\alpha\beta} = 0.$$

The solution of Eq. (2.28) is given by Eq. (2.29):

$$(2.29) \qquad q_\alpha^{(r)\beta} = -\frac{A^{(r)}}{b^{(r)}} \int\limits_{-\infty}^{t} G(t-\tau) C_{\alpha\beta}(\tau) d\tau.$$

Equation (2.14) in conjunction with Eqs. (2.27) and (2.29) leads to the constitutive equation

$$(2.30) \qquad \mathbf{T} + p\boldsymbol{\delta} = \mathbf{B}\frac{\partial \psi_0}{\partial \mathbf{B}} - \int\limits_{-\infty}^{t} G(t-\tau)\{\mathbf{B}^2(t)\mathbf{c}^{-1}(\tau) + \mathbf{c}^{-1}(\tau)\mathbf{B}(t)\}d\tau,$$

which has the following representation in the material system

$$(2.31) \qquad \tilde{\tau} + p\tilde{C} = 2\frac{\partial \psi_0}{\partial \mathbf{C}} - \int\limits_{-\infty}^{t} \{\tilde{C}(t)\mathbf{C}(\tau)\mathbf{C}(t) + \mathbf{C}(t)\mathbf{C}(\tau)\tilde{C}(t)\}G(t-\tau)d\tau.$$

Note the difference between Eqs. (2.21) and (2.30) on one hand and (2.24) and (2.31) on the other. It is worth emphasizing that this difference is brought about by the use of a different objective derivative. The free energy is the same in both cases.

Of course other choices of the objective derivative are possible. A third choice is the following:

$$(2.32) \qquad \hat{q}_{ij}^{(r)} = \dot{q}_{ij}^{(r)} - q_{kj}v_{i,k} + q_{ik}v_{k,j}$$

which has the material representation

$$(2.33) \qquad \dot{q}_\beta^{(r)\alpha} = x_i^\alpha y_{j\beta} \hat{q}_{ij}^{(r)},$$

where $q_\beta^{(r)\alpha}$ are the left mixed components of $\mathbf{q}^{(r)}$ given by the relation

$$(2.34) \qquad q_\beta^{(r)\alpha} = q_{ij}^{(r)} x_j^\alpha y_{i\beta}.$$

Equation (2.12) in conjunction with Eqs. (2.10), (2.32), (2.33) yields the set of r internal constitutive relations:

$$(2.35) \qquad C^{(r)} q_\beta^{(r)\alpha} + b^{(r)} \dot{q}_\beta^{(r)\alpha} + A^{(r)} C_{\alpha\beta} = 0.$$

These together with Eq. (2.14) lead to the constitutive equation:

$$(2.36) \qquad \mathbf{T} + p\boldsymbol{\delta} = 2B\frac{\partial \psi_0}{\partial \mathbf{B}} - 2\int\limits_{-\infty}^{t} G(t-\tau)\{\mathbf{B}(t)\mathbf{c}^{-1}(\tau)\mathbf{B}(t)\}d\tau$$

which, in the material system of coordinates becomes:

$$(2.37) \qquad \tilde{\tau} = 2\frac{\partial \psi_0}{\partial \mathbf{C}} - 2\int\limits_{-\infty}^{t} G(t-\tau)\mathbf{C}(\tau)d\tau - p\tilde{C}.$$

Certain physical implications of the above class of constitutive equations are worth discussing. Inspection of Eq. (2.14) shows that irrespective of how $q_{ij}^{(r)}$ depends on the deformation history, the stress components depend on the current deformation relative to the reference state, in the sense that at all finite times following the initiation of deformation T depends on $B(t)$. The material is, therefore, explicitly cognizant of its reference state; as such it is not a fluid.

The character of the above constitutive equations remains unchanged also in the case where the stress in the equilibrium state is a hydrostatic pressure. For instance it may be verified after integration by parts that the preceeding constitutive equations are of the general form

$$(2.38) \qquad T+p\delta = f(B) + \int_{-\infty}^{t} \big(\phi_1(B)\dot{c}^{-1}(\tau)\phi_2(B) + \phi_2(B)\dot{c}^{-1}(\tau)\phi_1(B)\big)G(t-\tau)d\tau,$$

where $B = B(t)$. Under conditions of relaxation

$$(2.39) \qquad \lim_{t\to\infty} T+p\delta = f(B).$$

Even if $f(B) = 0$, T depends explicitly on B for $t < \infty$. This implies that the material is cognizant of a specific reference configuration.

Constitutive equations which pertain to materials which are cognizant of a specific reference configuration, yet have an extremely short memory of their rate of deformation, are obtained by setting $f = 0$, and $G(t) = G_0 \delta(t)$ in Eq. (2.38). The result is

$$(2.40) \qquad T+p\delta = 2G_0[\phi_1 d\phi_2 + \phi_2 d\phi_1],$$

where ϕ_1 and ϕ_2 are isotropic functions of B.

3. Viscoelastic liquids

Evidently the above constitutive equations are inappropriate for materials in which the statistical molecular configuration in the equilibrium state is unaffected by previous deformation histories. Dilute polymer solutions are a case in point though the level of concentration and temperature at which are remarks are appropriate can be determined only by experiment.

To describe such materials we wish to derive constitutive equations in which T does not depend on $B(t)$ for all finite times following the initiation of deformation. Perusal of Eqs. (2.10) and (2.38) shows that the presence of B in the expression for the free energy gives rise to an explicit dependence of $T(t)$ on $B(t)$. The indicated procedure, therefore, is to make ψ independent of B. However, elimination of B from Eq. (2.38), would give rise to a zero stress, as Eq. (2.7) readily indicates.

The paradox is only apparent. It is the result of regarding the spatial components of $q^{(r)}$ as the independent variables. The difficulty is removed if the covariant, or contravariant components of $q^{(r)}$ are the independent variables instead, and due attention is given to the covariant (or contravariant) character of the aforesaid variables.

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To illustrate the point, we consider a free energy density which is quadratic function of $\mathbf{q}^{(r)}$. To wit, let

$$(3.1) \qquad \psi = \psi_0 + A^{(r)} q_{ii}^{(r)} + \frac{1}{2} C^{(r)} q_{ij}^{(r)} q_{ij}^{(r)},$$

where ψ_0, $A^{(r)}$ and $C^{(r)}$ are constants.

Fruther, let $q_{\alpha\beta}^{(r)}$ be the independent variables. In terms of these quantities equation (3.1) takes the form:

$$(3.2) \qquad \psi = \psi_0 + A^{(r)} q_{\alpha\beta}^{(r)} C^{\alpha\beta} + \frac{1}{2} C^{(r)} q_{\alpha\beta} q_{\alpha\delta} C^{\alpha\beta} C^{\beta\delta}.$$

Note the appearance of the inverse Right Cauchy Green tensor in the quadratic term on the right hand side of Eq. (3.2). This is contrast with Eq. (2.12) where $\mathbf{C}^{-1}$ does not appear in the quadratic term.

Because ψ now depends explicitly on $C^{\alpha\beta}$, it is convenient to write Eq. (2.7) in the form:

$$(3.3) \qquad \tau^{\alpha\beta} + p C^{\alpha\beta} = -2 C^{\alpha\beta} C^{\alpha\delta} \frac{\partial \psi}{\partial C^{\beta\delta}}.$$

If the material is "internally isotropic" then, for consistency, the rate of change of the covariant components $\dot{q}_{\alpha\beta}^{(r)}$ should be proportional to the covariant components of the internal stress tensor $\frac{\partial \psi}{\partial \mathbf{q}^{(r)}}$. The internal constitutive equations should, therefore, be of the form:

$$(3.4)_1 \qquad b^{(r)} \dot{q}_{\alpha\beta}^{(r)} + \frac{\partial \psi}{\partial q_{(r)}^{\alpha\beta}} = 0$$

or

$$(3.4)_2 \qquad b^{(r)} \dot{q}_{\alpha\beta}^{(r)} + C_{\alpha\mu} C_{\beta\nu} \frac{\partial \psi}{\partial q_{\mu\nu}^{(r)}} = 0.$$

Note that Eq. $(3.4)_2$ satisfies the Clausius-Duhem inequality

$$(3.4)_3 \qquad \frac{\partial \psi}{\partial q_{\alpha\beta}^{(r)}} \dot{q}_{\alpha\beta}^{(r)} \leqslant 0$$

since substitution of Eq. $(3.4)_2$ in $(3.4)_3$ yields the result:

$$(3.4)_4 \qquad C_{\alpha\mu} C_{\beta\nu} \frac{\partial \psi}{\partial q_{\mu\nu}^{(r)}} \frac{\partial \psi}{\partial q_{\alpha\beta}^{(r)}} \geqslant 0.$$

Inequality $(3.4)_4$ is true, since $b_r > 0$, and the term on the left hand side of the inequality, when represented in the spatial coordinate system, becomes:

$$(3.4)_5 \qquad \frac{\partial \psi}{\partial q_{ij}^{(r)}} \frac{\partial \psi}{\partial q_{ij}^{(r)}} \geqslant 0$$

which is of course a perfect square and therefore, non-negative.

Equation $(3.4)_2$ in conjunction with the quadratic form (3.2) yields the internal constitutive equation:

$$(3.5) \qquad A^{(r)} C_{\alpha\beta} + C^{(r)} q_{\alpha\beta}^{(r)} + b^{(r)} \dot{q}_{\alpha\beta}^{(r)} = 0.$$

Equation (3.5) may be integrated in the light of the condition that the material reference configuration is undisturbed' at $t = -\infty$ and that $\mathbf{q}^{(r)}|_{t=-\infty} = 0$ for all r, with the result that

$$(3.6) \qquad q_{\alpha\beta}^{(r)} = -\frac{A^{(r)}}{C^{(r)}} C^{\alpha\beta} + \frac{A^{(r)}}{C^{(r)}} \int_{-\infty}^{t} e^{-\alpha_r(t-\tau)} C_{\alpha\beta}(\tau)d\tau,$$

where $a_r = \dfrac{C^{(r)}}{b^{(r)}}$. Or, in the spatial frame of reference,

$$(3.7) \qquad q_{ij}^{(r)} = -\frac{A^{(r)}}{C^{(r)}} \delta_{ij} + \frac{A^{(r)}}{C^{(r)}} \int_{-\infty}^{t} e^{-\alpha_r(t-\tau)} \dot{c}_{ij}(\tau)d\tau.$$

On the other hand Eq. (3.3) gives rise to the following expression for the Cauchy stress:

$$(3.8) \qquad T_{ij} = -p\delta_{ij} - A^{(r)}q_{ij}^{(r)} - C^{(r)}q_{ik}^{(r)}q_{kj}.$$

Substitution of Eq. (3.7) in Eq. (3.8), yields readily the constitutive equation:

$$(3.9) \qquad T_{ij} = -p\delta_{ij} + \sum_r \frac{A^{(r)2}}{C^{(r)}} \int_{-\infty}^{t} e^{-\alpha_1 - (t-\tau)} \dot{c}(\tau)_{ij}d\tau$$

$$- \sum_r \frac{A^{(r)2}}{C_i} \int_{-\infty}^{t} e^{-\alpha_r(2t-\tau_1-\tau_2)} \dot{c}_{ik}(\tau_1)\dot{c}_{kj}(\tau_2)d\tau_1 d\tau_2.$$

Or, more compactly:

$$(3.10) \qquad \mathbf{T} = p\mathbf{\delta} + \int_{-\infty}^{t} G(t-\tau)\dot{\mathbf{c}}(\tau)d\tau - \int_{-\infty}^{t}\int_{-\infty}^{t} G(2t-\tau_1-\tau_2)\dot{\mathbf{c}}(\tau_1)\dot{\mathbf{c}}(\tau_1)d\tau_1 d\tau_2,$$

where

$$(3.11) \qquad G(t) = \sum_r \frac{A^{(r)2}}{C^{(r)}} e^{-(\alpha_r t)}.$$

Two points are worth mentioning with regard to the above equation: (i) the current left Cauchy Green tensor $\mathbf{B}(t)$ is absent; (ii) A double integral of the history of the relative Finger tensor is present even though the free energy density is quadratic in $q_{ij}^{(r)}$. Furthermore, the same function appears under both integrals thus making it impossible to eliminate the double integral by a suitable choice of parameters. Evidently, the constitutive equation (3.10) pertains to a material which has no memory of its reference configuration. The present stress, however, is a function of the deformation history relative to the current configuration. The material is therefore a fluid [13].

In a similar fashion the contravariant components of $\mathbf{q}^{(r)}$ may be considered as independent variables. In this case Eq. (3.1) now becomes:

$$(3.12) \qquad \psi = \psi_0 + A^{(r)}C_{\alpha\beta}q_{(r)}^{\alpha\beta} + \frac{1}{2} C^{(r)}q_{(r)}^{\alpha\beta}q_{(r)}^{\gamma\delta}C_{\alpha\gamma}C_{\beta\delta}.$$

In this case the stress is given by the equation

$$(3.13) \qquad \tau^{\alpha\beta} = 2\frac{\partial \psi}{\partial C_{\alpha\beta}} - pC^{\alpha\beta},$$

whereas the internal constitutive equations now are:

$$(3.14) \qquad \frac{\partial \psi}{\partial q_{\alpha\beta}^{(r)}} + b^{(r)}\dot{q}_{(r)}^{\alpha\beta} = 0.$$

Note again the balance of indices in equation (3.14). Following a procedure analogous to the foregoing we now find a constitutive equation of another type:

$$(3.15) \qquad T_{ij} = -p\delta_{ij} - \int\limits_{-\infty}^{t} G(t-\tau)\dot{c}_{ij}^{-1}(\tau)d\tau + \int\limits_{-\infty}^{t}\int\limits_{-\infty}^{t} G(2t-\tau_1-\tau_2)\,\dot{c}_{ik}^{-1}(\tau_1)\dot{c}_{kj}^{-1}(\tau_2)d\tau_1\,d\tau_2,$$

where

$$(3.16) \qquad G(t) = 2\sum_{r}\frac{A_r^2}{C_r}(e^{-\alpha_r t})$$

in the previous notation. The constitutive Eq. is now in terms of the inverse relative Finger strain tensor. Note again the absence from this equation of the left Cauchy-Green tensor $\mathbf{B}(t)$, which leads to the conclusion that the constitutive Eq. (3.15) pertains again to a fluid.

4. Endochronic fluids

In a previous series of papers, we discussed the concept of intrinsic time as it applies to solids. For such materials we stipulated that a distance between "deformation events" can be defined in a seven-dimensional space R, the coordinates of which consist of the six independent components of the Right Cauchy Green tensor and time. In particular, if the distance between two adjacent deformation events is $d\zeta$, then

$$(4.1) \qquad d\zeta^2 \overset{\text{def}}{=} P^{\alpha\beta\gamma\delta}dC_{\alpha\beta}dC_{\gamma\delta} + g^2dt^2,$$

where $P^{\alpha\beta\gamma\delta}$ may depend on $\mathbf{C}$. Alternatively,

$$(4.2) \qquad \left(\frac{d\zeta}{dt}\right)^2 = P^{\alpha\beta\gamma\delta}\dot{C}_{\alpha\beta}\dot{C}_{\gamma\delta} + g^2$$

the right hand side of Eq. (4.2) can be expressed in the spatial coordinate system in the form

$$(4.3) \qquad \left(\frac{d\zeta}{dt}\right)^2 = P_{ijkl}d_{ij}d_{kl} + g^2,$$

where

$$(4.3) \qquad P_{ijkl} = 4P^{\alpha\beta\gamma\delta}y_{i\alpha}y_{j\beta}y_{k\gamma}y_{l\delta};$$

conversely

$$(4.5) \qquad P^{\alpha\beta\gamma\delta} = \frac{1}{4}P_{ijkl}x_i^\alpha x_j^\beta x_k^\gamma x_l^\delta.$$

When dealing with fluids, which by definition have no preferred reference configuration, the "intrinsic tensor" P_{ijkl} cannot depend on the present deformation relative to the reference state, i.e., on $B_{ij}(t)$. In order to apply the theory to fluids and to keep the analysis tractable we shall assume, in this paper, that $\mathbf{P}$ is at most an isotropic tensor function of d_{ij}. In this event Eq. (4.3) can be written more concisely in the form:

(4.6)
$$\left(\frac{d\zeta}{dt}\right)^2 = f(d_1, d_{11}, d_{111}) + g^2,$$

where

$$d_M = \operatorname{tr}(\mathbf{d}^M), \quad M = I, II, III.$$

In the case of incompressible liquids $d_1 = 0$, and

(4.7)
$$f = f(d_{11}, d_{111}).$$

As a consequence of Eq. (4.1), a deformation history is mapped into the space R as a path. The length of an element of this path, is $d\zeta$, where $d\zeta^2$ is given by Eq. (4.1). Evidently the space R is not Euclidean, but Riemannian with a metric $\mathbf{G}$, where;:

(4.8)
$$\mathbf{G} = \begin{pmatrix} \mathbf{P} & 0 \\ 0 & g^2 \end{pmatrix}.$$

Consider now a typical internal variable $\mathbf{q}^{(r)}$, the values of which may be computed along a path in R, i.e., $\mathbf{q}^{(r)} = \mathbf{q}^{(r)}(\zeta)$. The intrinsic rate of change of $\mathbf{q}^{(r)}$ along the path is $\dfrac{d\mathbf{q}^{(r)}}{d\zeta}$.

As an extension of the theory of internal variables we stipulate that

(4.9)
$$\frac{\partial \psi}{\partial \mathbf{q}^{(r)}} + \tilde{\tilde{b}}^{(rs)} \cdot \frac{d\mathbf{q}^{(s)}}{d\zeta} = 0.$$

Equations such as (4.9) constitute *endochronic fluids* since their constitutive equations are expressed in terms of an internal time scale which is a property of the fluid at hand. The contravariant viscocity tensors $\tilde{\tilde{b}}^{(rs)}$ are all positive semi-definite; further, the set of elements (r, s) corresponding to a particular component of the tensor $\tilde{\tilde{b}}^{(rs)}$, constitutes a positive semi-definite matrix.

It is conceivable that to each internal variable $\mathbf{q}^{(r)}$ there corresponds an intrinsic time scale ζ_r. In this sense it may said that a material possesses an intrinsic time spectrum $\zeta_r, r-1, 2, \ldots, n$.

In terms of such a spectrum there does exist a set [*] of internal constitution equations of the type:

(4.10)
$$\frac{\partial \psi}{\partial \mathbf{q}^{(r)}} + b^{(rs)} \cdot \frac{d\tilde{q}^{(s)}}{d\zeta_s} \quad (s \text{ summed}),$$

where

(4.11)
$$d\zeta_s^2 = d\mathbf{C} \cdot \mathbf{P}^s \cdot d\mathbf{C} + g_s^2 dt^2,$$

---

[*] This is a particular set for a proper choice of $\tilde{\tilde{b}}$. See Eq. (4.13).

or recalling Eq. (4.6):

$$(4.12) \qquad \left(\frac{d\zeta_s}{dt}\right)^2 = f_s(d_I, d_{II}, d_{III}) + g_s^2.$$

The internal variable theory with an intrinsic time spectrum is now complete.

We proceed to solve Eq. (4.10) when the free energy is given by quadratic form (3.1) and the Cartesian components of **b** are given in Eq. (4.13)

$$(4.13) \qquad b_{ijkl}^{(r)} = b_0^{(r)} \delta_{ik} \delta_{jl},$$

where $b_0^{(r)}$ are constants. If the covariant components of $q^{(r)}$ are used as independent variables one obtains by the procedure of Sect. 3, the constitutive Eq. (4.14):

$$(4.14) \quad \mathbf{T} = -p\boldsymbol{\delta} + \sum_{r=1}^{n} \frac{A^{(r)2}}{C^{(r)}} \int_{-\infty}^{\zeta_r} e^{-\alpha_r(\zeta_r - \zeta_r')} \frac{\partial \mathbf{c}}{\partial \zeta_r'} d\zeta_r'$$

$$- \sum_{r=1}^{n} \frac{A^{(r)2}}{C^{(r)}} \int_{-\infty}^{\zeta_r} \int_{-\infty}^{\zeta_r} e^{-\alpha_r(2\zeta_r - \zeta_r' - \zeta_r'')} \frac{\partial \mathbf{c}}{\partial \zeta'} \frac{\partial \mathbf{c}}{\partial \zeta''} d\zeta_r' d\zeta_r''.$$

This equation is similar to the Bird-Carreau Eq. (2.18) except for the presence of the double integral, which incidentally cannot be eliminated, because the constants and relaxation times therein are precisely those of the first integral.

In a similar fashion, if the contravariant components of $\tilde{q}^{(r)}$ are considered to be the independent variables, in this case one obtains Eq. (4.15):

$$(4.15) \quad T_{ij} = -p\delta_{ij} - \sum_{r=1}^{n} \frac{A^{(r)2}}{C^{(r)}} \int_{-\infty}^{\zeta_r} e^{-\alpha_r(\zeta_r - \zeta_r')} \frac{\partial c_{ij}^{-1}}{\partial \zeta_r'} d\zeta_r'$$

$$+ \sum_{r=1}^{n} \frac{A^{(r)2}}{C^{(r)}} \int_{-\infty}^{\zeta_r} \int_{-\infty}^{\zeta_r} e^{-\alpha_r(2\zeta_r - \zeta_r' - \zeta_r'')} \frac{\partial c_{ik}^{-1}}{d\zeta_r'} (\zeta_r') \frac{\partial c_{kj}^{-1}}{\partial \zeta_r''} (\zeta_r') d\zeta_r' d\zeta_r''.$$

Of course it may happen that at set k of internal variables, $q_1^{(r)}, q_2^{(r)} \ldots q_k^{(r)}$, share one and the same intrinsic time scale ζ_r. In this event Eqs. (4.14) and (4.15) can be readily generalized as shown below. In particular Eq. (4.14) will become:

$$(4.16)$$
$$\mathbf{T} = -p\boldsymbol{\delta} + \sum_{n} \int_{-\infty}^{\zeta_r} G_r(\zeta - \zeta_r') \frac{\partial \mathbf{c}}{\partial \zeta_r'} d\zeta_r' - \sum_{n} \int_{-\infty}^{\zeta_r} \int_{-\infty}^{\zeta_r} G_r(2\zeta_r - \zeta_r' - \zeta_r'') \frac{\partial \mathbf{c}}{\partial \zeta_r'} \frac{\partial \mathbf{c}}{\partial \zeta_r'} d\zeta_r' d\zeta_r''.$$

In a similar fashion Eq. (4.17) will become:

$$(4.17) \quad \mathbf{T} = -p\boldsymbol{\delta} - \sum_{n} \int_{-\infty}^{\zeta_r} G_r(\zeta - \zeta_r') \frac{\partial \mathbf{c}}{\partial \zeta_r'} d\zeta_r' + \sum_{n} \int_{-\infty}^{\zeta_r} \int_{-\infty}^{\zeta_r} G_r(2\zeta_r - \zeta_r' - \zeta_r'')$$

$$\times \frac{\partial \mathbf{c}^{-1}}{\partial \zeta_r'} \frac{\partial \mathbf{c}^{-1}}{\partial \zeta_r''} d\zeta_r' d\zeta_r''.$$

These equations are of a generality in excess of those by BIRD, CARREAU [18] White, Bogue and others.

Acknowledgment

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DIVISION OF MATERIALS ENGINEERING,
UNIVERSITY OF IOWA, IOWA CITY, IOWA.