On the Determination of Free Energy in Linear Viscoelastic Solids[1])

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1. Introduction

Consider *isothermal* deformations of a linear viscoelastic solid in simple tension or compression. Let $\sigma(t)$ and $\varepsilon(t)$ denote, respectively, the relevant stress and infinitesimal strain components at time t. We adopt the stress-strain law in the form [1][4])

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} \, d\tau \,, \tag{1}$$

where $G(t)$ is the relaxation modulus. We shall restrict our attention in the following to the class of relaxation moduli defined by

$$G(t) = \sum_{i=1}^{N} c_i \, e^{-a_i t} \quad \text{for} \quad t \geq 0 \,, \tag{2}$$

where c_i and a_i are positive constants and $a_i < a_{i+1}$.

The paper is concerned with the study of the free energy F and the entropy production θ in the solid defined by (1) and (2). Our point of departure is the thermodynamic equation

$$\sigma(t) \, \dot{\varepsilon}(t) = \dot{F} + T_0 \, \dot{\theta} \,, \tag{3}$$

where the dot indicates the time rate of change of the quantities concerned at time t, and T_0 is the (constant) temperature of the element. This equation is obtained from the energy equation (the first law of thermodynamics) and the equation of entropy balance[5]). The second law of thermodynamics requires that the rate of entropy production be non-negative definite:

$$\dot{\theta} \geq 0 \,. \tag{4}$$

We shall assume that F and θ are functionals of the strain rate history to which the material element under consideration has been subjected. We now inquire whether the knowledge of the relaxation modulus (2) will enable us to determine these two functionals, with the help of the constitutive relation (1), the thermodynamic Equation (3) and the second law (4). This problem has been studied by STAVERMAN and SCHWARZL [2], BLAND [3] and HUNTER [4], whose point of departure has been to regard the viscoelastic material as consisting of a network of linear viscous and

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[4]) Numbers in square brackets refer to References, page 191.

[5]) See the Appendix.

elastic elements, i.e. dashpots and springs. Pursuing the idea of model representation, these authors, in independent works, arrived at the following expression for the free energy (per unit volume) of the solid:

$$\overset{t}{\underset{-\infty}{F_1}} = \frac{1}{2}\int_{-\infty}^{t}\int_{-\infty}^{t} G(2\,t - \tau_1 - \tau_2)\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2\,, \tag{5}$$

where $\dot{\varepsilon}(\tau)$ is the strain rate history to which the solid has been subjected in the interval $-\infty < \tau \leq t$, and $G(t)$ is the given relaxation modulus represented by (2). An expression similar to (5) has also been given by the above authors for the rate of entropy production at time t[6]).

A remarkable aspect of the second order functional in (5) is that it depends on the given relaxation modulus, but not on the type of model chosen to derive this expression. This remark suggests the possibility that the functional (5), representing the free energy of the solid, may be obtained without using a model representation. The paper is concerned with a discussion of this possibility.

It is shown that the conditions we are able to impose on F, without recourse to model representation, reduce the general form of F discussed in the next section to a much simpler form, but they fail to determine F uniquely. In the last section we construct a model contraining a mass for which the free energy is different from the one given in (5).

2. The General Form of the Free Energy

As a first step toward the determination of F we shall assume that it can be represented as a functional of the given strain rate history in the following manner,

$$\overset{t}{\underset{-\infty}{F}} = \int_{-\infty}^{t}\int_{-\infty}^{t} K(t - \tau_1, t - \tau_2)\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2\,, \tag{6}$$

where $K(x, y)$ is a continuous, symmetric kernel, whose first partial derivatives with respect to x and y exist. We shall also assume that $\overset{t}{\underset{-\infty}{F}}$ is non-negative definite i.e.

$$\overset{t}{\underset{-\infty}{F}} \geq 0\,, \tag{7}$$

so that $K(x, y)$ must be a non-negative definite kernel. We now differentiate (6) with respect to t and make use of the thermodynamic relation (3), to obtain

$$\sigma(t)\,\dot{\varepsilon}(t) = 2\,\dot{\varepsilon}(t)\int_{-\infty}^{t} K(0, t - \tau)\,\dot{\varepsilon}(\tau)\,d\tau + \int_{-\infty}^{t}\int_{-\infty}^{t} \frac{\partial K}{\partial t}\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2 + T_0\,\dot{\theta}\,. \tag{8}$$

[6]) It must be noted that F_1 represents the sum of the free energies of the elastic elements in the model. The expression given by the above authors for the rate of entropy production, on the other hand, corresponds to the sum of energy dissipation in the viscous elements. It is of interest to note that $T_0\,\dot{\theta}$ cannot, in general, be interpreted as the rate of heat production in the element considered since the isothermal deformations of elastic elements of the model will in general require heat exchange with the surrounding medium. However, in cases where this heat exchange is negligible, $T_0\,\dot{\theta}$ can be identified as the rate of heat production in the considered element.

We make the further assumptions that $\sigma(t)$ as well as $\dot{\theta}$ do not depend upon $\dot{\varepsilon}(t)$ [7]. It then follows from (8) that

$$\sigma(t) = 2\int_{-\infty}^{t} K(0, t-\tau)\,\dot{\varepsilon}(\tau)\,d\tau\,, \tag{9}$$

$$T_0\,\dot{\theta} = -\int_{-\infty}^{t}\int_{-\infty}^{t} \frac{\partial K}{\partial t}\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2\,. \tag{10}$$

The preceding analysis may now be seen to result in the following three conditions upon the unknown kernel $K(x, y)$:

By (6) and (7) we must have

$$\overset{t}{\underset{-\infty}{F}} = \int_{-\infty}^{t}\int_{-\infty}^{t} K(t-\tau_1, t-\tau_2)\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2 \geq 0\,, \tag{11}$$

for all $\dot{\varepsilon}(\tau)$. From (4) and (10) we find

$$T_0\,\dot{\theta} = -\int_{-\infty}^{t}\int_{-\infty}^{t} \frac{\partial K}{\partial t}\,\dot{\varepsilon}(\tau_1)\,\dot{\varepsilon}(\tau_2)\,d\tau_1\,d\tau_2 \geq 0\,, \tag{12}$$

for all $\dot{\varepsilon}(\tau)$. Finally, (9) and (1) yield

$$K(0, t) = \frac{1}{2}\,G(t)\,. \tag{13}$$

As will be apparent from subsequent results, the knowledge of $G(t)$, supplemented by the conditions (11), (12) and (13), is not sufficient to determine the general form of $K(x, y)$ and hence of F. We must therefore seek further conditions which F must satisfy. To this end, suppose the material is subjected to a straining program $\varepsilon(\tau)$, in $(-\infty, \infty)$, with the following properties:

$$\dot{\varepsilon}(\tau) = 0 \quad \text{for} \quad \tau < -T \quad \text{and} \quad \tau > 0\,, \tag{14}$$

and

$$\int_{-T}^{0} G(t-\tau)\,\dot{\varepsilon}(\tau)\,d\tau = 0 \quad \text{for} \quad t \geq 0\,, \tag{15}$$

where T is a fixed positive number. Combining (14) and (15) with (1) and (2) we obtain

$$\sigma(t) = \sum_{i=1}^{N} c_i\,e^{-a_i t}\int_{-T}^{0} e^{a_i\tau}\,\dot{\varepsilon}(\tau)\,d\tau = 0 \quad \text{for} \quad t \geq 0\,. \tag{16}$$

Now (16) will hold if and only if

$$\int_{-T}^{0} e^{a_i\tau}\,\dot{\varepsilon}(\tau)\,d\tau = 0, \quad i = 1, 2, \ldots, N\,, \tag{17}$$

[7] Note that the first assumption is equivalent, in view of (1), to the assumption that $G(t)$ is continuous in the interval $0 \leqq t < \infty$.

because the functions $e^{-a_i t}$ are linearly independent. On the other hand, the linear independence of the functions $e^{a_i \tau}$ guarantees that it is always possible to find non-trivial $\dot{\varepsilon}(\tau)$ such that (17) will hold. Thus the straining program described by (14)–(15) can be realized.

We now observe, that under the straining program just described the material will be in a completely relaxed state, with zero stress and constant strain for $t \geq 0$. Indeed, an observer who is given the material for $t \geq 0$, will not be able to distinguish it from a virgin material. Thus we demand that the free energy of the material subjected to a straining program given by (14)–(15) shall be zero for $t \geq 0$. It follows now from (11), (14) and (15) that

$$\overset{t}{\underset{-\infty}{F}} = \int_{-T}^{0} \int_{-T}^{0} K(t-\tau_1, t-\tau_2)\, \dot{\varepsilon}(\tau_1)\, \dot{\varepsilon}(\tau_2)\, d\tau_1\, d\tau_2 = 0 \quad \text{for} \quad t \geq 0\,, \tag{18}$$

if (17) holds. In particular, (18) must hold at $t = 0$. Putting $t = 0$ in (18) and writing

$$f(x) = \dot{\varepsilon}(-x)\,, \tag{19}$$

we have from (17), (18) and (19) the additional condition to be satisfied by $K(x, y)$ in the form

$$\int_0^T \int_0^T K(x, y)\, f(x)\, f(y)\, dx\, dy = 0\,, \tag{20}$$

whenever

$$\int_0^T e^{-a_i x} f(x)\, dx = 0, \quad i = 1, 2, \ldots, N\,. \tag{21}$$

We may now make use of (20) and (21) to determine the general form of $K(x, y)$. Since $K(x, y)$ is a continuous, non-negative definite kernel, Mercer's theorem[8]) gives the uniformly convergent expansion

$$K(x, y) = \sum_{n=1}^{\infty} \frac{\varphi_n(x)\, \varphi_n(y)}{\lambda_n}\,, \tag{22}$$

where λ_n are the (positive) eigenvalues and φ_n the corresponding (real) eigenfunctions associated with the kernel $K(x, y)$ in the interval $(0, T)$. Since $\lambda_n > 0$, due to the non-negative definiteness of $K(x, y)$, we obtain from (20) and (22) that for $f(x)$ satisfying (21),

$$\int_0^T \varphi_n(x)\, f(x)\, dx = 0, \quad n = 1, 2, \ldots\,. \tag{23}$$

In view of (21), (23) expresses the fact that $\varphi_n(x)$ must be orthogonal, in the interval $(0, T)$, to any function $f(x)$ which is orthogonal to $e^{-a_i x}$ in the same interval. This observation implies, as the following argument shows, that $\varphi_n(x)$ must be of the form

$$\varphi_n(x) = \sum_{i=1}^{N} \gamma_{n\,i}\, e^{-a_i x}\,, \tag{24}$$

[8]) See [5], p. 138.

where $\gamma_{n i}$ are constants. In order to prove (24), we may decompose $\varphi_n(x)$ in the form

$$\varphi_n(x) = \sum_{i=1}^{N} \gamma_{n i} \, e^{-a_i x} + \psi_n(x) , \quad n = 1, 2, \ldots , \tag{25}$$

where $\psi_n(x)$ are chosen, without loss of generality, to be orthogonal to $e^{-a_i x}$ in $(0, T)$, i.e.

$$\int_0^T e^{-a_i x} \, \psi_n(x) \, dx = 0 , \quad i = 1, 2, \ldots , N ; \quad n = 1, 2, \ldots . \tag{26}$$

Multiplying (25) by $f(x)$, integrating from 0 to T, and using (21) as well as (23), we find

$$\int_0^T \psi_n(x) \, f(x) \, dx = 0 , \quad n = 1, 2, \ldots . \tag{27}$$

In view of (26), $\psi_n(x)$ is a function which satisfies the restriction (21) imposed on $f(x)$. Thus in (27), $f(x)$ may be replaced by $\psi_n(x)$ – to obtain the desired result, $\psi_n = 0$, $n = 1, 2, \ldots$.

Since the eigenfunctions $\varphi_n(x)$ are linearly independent, (24) shows that there can be no more than N of them. Consequently, the kernel $K(x, y)$ is degenerate, and we find from (22) and (24) that

$$K(x, y) = \sum_{i=1}^{N} \sum_{j=1}^{N} \beta_{i j} \, e^{-a_i x - a_j y} , \tag{28}$$

where $\beta_{i j}$ are symmetric constants due to the symmetry of $K(x, y)$. Our considerations are restricted so far to the domain $0 \leq x, y \leq T$, so that $\beta_{i j}$ may, in principle, depend on T. However, since T is an arbitrary positive constant one can show by a simple argument that $\beta_{i j}$ cannot depend on T. Finally, in so far as (28) has been derived on the basis of evaluating (18) at $t = 0$, we have yet to verify that (18) will indeed be satisfied for all $t \geq 0$ if $K(x, y)$ is given by (28). A trivial calculation shows that such is indeed the case.

Having found the general form of $K(x, y)$ as given by (28), we return to the conditions (11)–(13) derived earlier. It will be expedient to define the following functionals of $\dot{\varepsilon}(\tau)$:

$$K_i = \int_{-\infty}^{t} e^{-a_i (t - \tau)} \, \dot{\varepsilon}(\tau) \, d\tau, \quad i = 1, 2, \ldots , N . \tag{29}$$

In terms of K_i we find that (11) and (28) may be combined to give

$$\underset{-\infty}{\overset{t}{F}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \beta_{i j} \, K_i \, K_j \geq 0 , \tag{30}$$

while (12) and (28) yield

$$T_0 \, \dot{\theta} = \sum_{i=1}^{N} \sum_{j=1}^{N} (a_i + a_j) \, \beta_{i j} \, K_i \, K_j \geq 0 . \tag{31}$$

Finally, (13), (2) and (28), together with the linear independence of $e^{-a_i x}$, furnish

$$\sum_{j=1}^{N} \beta_{i j} = \frac{1}{2} \, c_i, \quad i = 1, 2, \ldots , N ; \quad (\beta_{i j} = \beta_{j i}) . \tag{32}$$

It can easily be seen that for $N > 1$ the Equations (32) and the inequalities (30) and (31) do not suffice to determine β_{ij} uniquely[9]). (32) represent N equations for $N(N+1)/2$ unknowns, and the inequalities (30) and (31) fail to limit, in some significant way, the remaining $N(N-1)/2$ unknowns. In order to see this in an explicit fashion we consider the special case of $N = 2$. Using (32) and the well known necessary and sufficient conditions[10]) for the positive definiteness of the quadratic forms (30) and (31), we obtain the following inequalities for β_{12},

$$\beta_{12} < \frac{1}{2} \min (c_1, c_2) , \quad \beta_{12} < \frac{1}{2} \frac{c_1 c_2}{c_1 + c_2} , \tag{33}$$

and

$$-\frac{A+B}{(a_2 - a_1)^2} < \beta_{12} < \frac{A-B}{(a_2 - a_1)^2} , \tag{34}$$

where

$$B = a_1 a_2 (c_1 + c_2) > 0 , \quad A = [B^2 + a_1 a_2 c_1 c_2 (a_2 - a_1)^2]^{1/2} > B. \tag{35}$$

It is easily seen that (33) are implied by (34). Indeed, using (35) we obtain the following successive relations,

$$\left.\begin{aligned} \frac{A-B}{(a_2-a_1)^2} &= \frac{A^2 - B^2}{(A+B)(a_2-a_1)^2} = \frac{a_1 a_2 c_1 c_2}{A+B} \\ &< \frac{a_1 a_2 c_1 c_2}{2B} = \frac{1}{2} \frac{c_1 c_2}{c_1 + c_2} < \frac{1}{2} \min (c_1, c_2) . \end{aligned}\right\} \tag{36}$$

Hence (34) is the only restriction on β_{12} *and it fails to determine* β_{12} *uniquely.*

Before closing this section we wish to point out that F may be written, with the aid of (32), in the following form,

$$\overset{t}{\underset{-\infty}{F}} = \frac{1}{2} \sum_{i=1}^{N} c_i K_i^2 - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \beta_{ij} (K_i - K_j)^2 , \tag{37}$$

where β_{ij} are subject to inequalities of the type discussed for the case $N = 2$. It is interesting to observe, with the help of (29) and (2), that the first term on the right hand side of (37) is identical with the expression (5) given by the above mentioned authors; i.e. their result would agree with our result if β_{ij} were zero for $i \neq j$.

The conditions that we were able to impose on F, without recourse to model representation, reduce the general form (11) to the simpler form (37), but they prove to be short of reducing F to the form given by (5). In the next section we construct a model for which the expression for the free energy is different from (5), yet conforms to (37).

3. *Example:* In this section we briefly discuss an example of two models having identical relaxation moduli but differing in their free energies. Consider first two

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[9]) For $N = 1$, i.e. when the material is a Maxwell body, (32) and (28) yield

$$K(x, y) = \frac{1}{2} c_1 e^{-a_1 (x+y)} ,$$

and in a similar manner, (32) and (30) give

$$\overset{t}{\underset{-\infty}{F}} = \frac{1}{2} c_1 K_1^2 .$$

[10]) See [6], p. 137.

Maxwell elements connected in parallel. For this model it is well known that the relaxation modulus is given by

$$G(t) = c_1 e^{-a_1 t} + c_2 e^{-a_2 t}, \tag{38}$$

where c_i and c_i/a_i $(i = 1, 2)$ are the spring constants and dashpot viscosities, respectively. The free energy of the springs is easily seen to be

$$F_1 = \frac{1}{2} c_1 K_1^2 + \frac{1}{2} c_2 K_2^2, \tag{39}$$

where K_i is given by (29). This corresponds to (37) with $N = 2$, $\beta_{12} = 0$, and hence is in accord with (5).

On the other hand, consider the modified model in which a mass m is inserted between the spring and the dashpot of *one* of the two Maxwell elements. Let d_1 and μ_1 be the spring constant and dashpot viscosity of the element containing the mass, d_2 and μ_2 having analogous meaning for the mass-free Maxwell element. It can be shown then that d_i and μ_i $(i = 1, 2)$ can be so chosen that the relaxation modulus of this model is again given by (38).

The free energy of the resulting model is the sum of the energy of the springs and the kinetic energy of the mass, and may be shown to be

$$F = \frac{1}{2} c_1 K_1^2 + \frac{1}{2} c_2 K_2^2 + \frac{d_1^2}{m (a_2 - a_1)^2} (K_1 - K_2)^2 . \tag{40}$$

Comparison of (40) with (37) shows that for this model

$$\beta_{12} = - \frac{d_1^2}{m (a_2 - a_1)^2} . \tag{41}$$

Moreover, it can easily be shown that β_{12}, as given in (41), satisfies the inequalities (34).

This example shows that the relaxation modulus is not sufficient to determine the free energy uniquely beyond the form (37) supplemented by the inequalities implicit in (30) and (31).

Appendix

Consider deformations of a linear isotropic viscoelastic solid. Let $\sigma_{ij}(x, t)$ and $\varepsilon_{ij}(x, t)$ denote, respectively, the components of the stress and infinitesimal strain tensors at time t and position x, where x stands for the triplet of coordinates (x_1, x_2, x_3) in a rectangular cartesian coordinate system.

Let the material occupy the finite regular domain D whose boundary is denoted by B. If the material is deformed, the first law of thermodynamics states that[11])

$$\sigma_{ij} \dot{\varepsilon}_{ij} = \dot{e} + \frac{\partial q_i}{\partial x_i}, \tag{42}$$

where e is the internal energy per unit volume of the solid and q_i are the components of the heat flux vector.

Let n_i denote the components of the unit outward normal to B. The equation of entropy balance may be written in the form

$$\int_D \dot{S} d V = - \int_B \frac{1}{T} q_i n_i dA + \int_D \dot{\eta} dV , \tag{43}$$

[11]) See, for example, [7], p. 244.

where S is the entropy per unit volume and T is the temperature. The first term on the right of (43) represents the rate at which entropy is supplied to the solid across its boundary, while $\dot{\eta}$ is the rate of entropy production per unit volume of the solid. Using the Divergence theorem, (43) gives

$$T\,\dot{S} = -\frac{\partial q_i}{\partial x_i} + \frac{1}{T}\,q_i\,\frac{\partial T}{\partial x_i} + T\,\dot{\eta}\,. \tag{44}$$

Now the rate of entropy production may be split as follows

$$\dot{\eta} = -\frac{1}{T^2}\,q_i\,\frac{\partial T}{\partial x_i} + \dot{\theta}\,, \tag{45}$$

where the first term on the right is identified with the rate of entropy production due to heat conduction whereas the second term represents the rate of entropy production due to internal processes. It follows now from (42), (44) and (45) that

$$\sigma_{ij}\,\dot{\varepsilon}_{ij} = \dot{e} + T(\dot{\theta} - \dot{S})\,. \tag{46}$$

At this point we introduce the (HELMHOLTZ) free energy F, defined by

$$F = e - T\,S\,. \tag{47}$$

Assuming isothermal conditions, i.e. $T = T_0$,

$$\dot{F} = \dot{e} - T_0\,\dot{S}\,, \tag{48}$$

so that (48) and (46) give

$$\sigma_{ij}\,\dot{\varepsilon}_{ij} = \dot{F} + T_0\,\dot{\theta}\,. \tag{49}$$

For simple tension or compression, (49) gives way to

$$\sigma\,\dot{\varepsilon} = \dot{F} + T_0\,\dot{\theta}\,.$$

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Zusammenfassung

Der Artikel behandelt die isotherme Verformung eines linear-viskoelastischen Stoffes im einachsigen Spannungszustand. Ein Integralgesetz für die Spannungs-Dehnungsbeziehung wird aufgestellt, in dem der Relaxationsmodul als Summe von Exponentialfunktionen angesetzt wird. Die Möglichkeit, die freie Energie und die Entropieproduktion aus der Kenntnis des Relaxationsmoduls zu bestimmen, wird diskutiert. Im Gegensatz zu früheren Untersuchungen dieses Problems macht der vorliegende Artikel keinen Gebrauch von Modellvorstellungen und stützt sich ausschliesslich auf thermodynamische Überlegungen.

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