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# UNIQUE CHARACTERIZATION OF MATERIALS WITH MEMORY

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ABSTRACT. In general, materials with linear memory constitutive relations are characterized by a relaxation function. This leads to a situation where the free energy for most materials with memory is not unique. There is a convex set of free energy functionals with a minimum and a maximum element. An alternative procedure is proposed which characterizes a material by the kernel of the rate of dissipation functional. Using some recent results, we find that a unique free energy and relaxation function may then be deduced.

An example is given for discrete spectrum materials. Also, the new results are used to show that a previously derived general representation of rate of dissipation and free energy functionals is not complete, in the sense that there are valid functionals which cannot be described by this general formula.

## 1. INTRODUCTION.

A very general feature of materials with memory, both linear and non-linear, is that free energy functionals are not unique. They form a bounded convex set with a minimum and a maximum element ([7], [1] and references therein). The minimum free energy associated with a given state is equal to the maximum recoverable work from that state, while the maximum free energy is the minimum energy required to achieve the state.

We are considering a material with a constitutive equation that has a linear memory term, in other words, a memory contribution that is a linear functional of the strain history. Such materials are generally characterized by a relaxation function, and it can be shown that the minimum and maximum free energies can be expressed in terms of quantities derivable from that relaxation function. Indeed, all expressions for free energy functionals obtained so far have been explicitly expressed in terms of the relaxation function of the material, or indirectly so ([1] and older publications given therein; also, recent papers [2, 12, 13, 14]).

Since there are generally many free energy kernels which yield a given relaxation function, this leads to a situation where there are many free energies and rates of dissipation associated with a given material in a particular state. This is the mechanism whereby the non-uniqueness of free energy and rate of dissipation functionals can be understood in the context of linear memory materials. Such non-uniqueness means that there is no clear method of identifying which is the physical free energy and rate of dissipation, though a proposal on this issue has been made [10, 11].

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The set of such free energy and rate of dissipation functionals associated with a linear memory material will be denoted by  $\mathcal{F}$ .

For simplicity, isothermal mechanical problems, indeed those for solid viscoelastic materials, will be considered here; also, only the scalar case is explored, which simplifies the algebra and allows us to focus on the essential structure of the arguments. It must be emphasized however that similar results can be given, with little extra difficulty, for viscoelastic fluids, some non-isothermal problems, electromagnetic and non-simple materials with memory, and also for the general tensor theories relating to all of these.

Recent work [12] seeks to systematically explore existing and new categories of free energy functionals, using a novel technique. This method is based on a result showing that if a suitable kernel for the rate of dissipation is known, the associated free energy kernel can be determined by a straightforward formula, yielding a non-negative quadratic form. It allows us to determine previously unknown free energy functionals by hypothesizing rates of dissipation that are non-negative, and applying the formula. In particular, new free energy functionals related to the minimum free energy are constructed.

The central results of [12] form the basis of the proposal presented here, which is that the natural characterization of a material with memory is not the relaxation function, but rather the kernel of the rate of dissipation functional. This new approach leads to a unique, valid, free energy, and provides a formula for the relaxation function. Thus, it is a complete characterization of the material. Of course, we are not referring to a real material, but rather a mathematical model, approximately describing some aspects of the behaviour of a real material.

The standard approach is to specify the relaxation function and seek free energy functionals either explicitly dependent on this quantity, or through a factorization process on a function derivable from it. The first method is applicable only if this relaxation function is a monotonically decaying quantity, while the second approach yields the minimum and related free energies, which lie on the boundaries of  $\mathcal{F}$ . However, since we cannot determine the physically correct choice, this approach provides a complete description of constitutive behaviour in the sense of stress-strain relations, but gives at best a partial characterization of energy storage and dissipation.

The basic argument on which we base this work is a simplified version of that presented in section 6.1.3 of [1]. One practical problem with the new approach is that the kernel of the rate of dissipation functional is difficult to measure, particularly in a non-isothermal context. For an isothermal problem, it is the amount of heat produced by work on the material<sup>1</sup>. The issue of measurement is briefly discussed in [1]. It may be that the determination of the kernel in the frequency domain is a more practical approach, just as for the complex modulus measurements related to the relaxation function.

The issue of minimal states is not discussed in the present work. Recent results on this topic may be found in [4].

Regarding the notational convention for referring to equations, we adopt the following rule. A group of relations with a single equation number (\*\*\*) will be individually labeled by counting “=” signs or “<”, “>”, “≥” and “≤”. Thus, (\*\*\*)<sub>5</sub>

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<sup>1</sup>Such a material, together with its immediate environment must be good heat conductors, so as to prevent a significant local increase in temperature.

refers to the fifth “=” sign, if all the relations are equalities. Relations with “ $\subset$ ” are ignored for this purpose.

Various formulae are used in this work which are derived in several earlier publications. Derivations are therefore omitted, though, in some cases, a relevant reference is given.

## 2. BASIC RELATIONSHIPS

The strain at time  $t$  and its history are  $E(t)$  and  $E^t$  respectively, where

$$E^t(s) = E(t - s), \quad s \in \mathbb{R}^+, \quad (2.1)$$

while the relative history is given by

$$E_r^t(s) = E^t(s) - E(t), \quad s \in \mathbb{R}^+. \quad (2.2)$$

For simplicity, we take the history to be continuous, in particular at  $s = 0$ . The stress is denoted by  $T(t)$ . The general form of the constitutive relation is

$$T(t) = \tilde{T}(E^t, E(t)), \quad (2.3)$$

where it is understood that  $\tilde{T}$  is a functional of  $E^t$  and a function of  $E(t)$ . The general form of a free energy functional is denoted by

$$\psi(t) = \tilde{\psi}(E^t, E(t)) \geq 0, \quad (2.4)$$

where, as with  $\tilde{T}$ , the quantity  $\tilde{\psi}$  is a functional of  $E^t$  and a function of  $E(t)$ . Let  $E^\dagger$  be the static history, equal to  $E(t)$  at the current and all past times. Then

$$\tilde{\psi}(E^\dagger, E(t)) = \tilde{\phi}(E(t)) = \phi(t) \geq 0, \quad (2.5)$$

where  $\tilde{\phi}(E(t))$  is the equilibrium free energy.

The fundamental properties of free energies are now summarized [5, 7, 15, 16, 1]. We must have

$$\frac{\partial \tilde{\psi}(E^t, E(t))}{\partial E(t)} = \frac{\partial \psi(t)}{\partial E(t)} = T(t) = \tilde{T}(E^t, E(t)). \quad (2.6)$$

Also, for any history and current value  $(E^t, E(t))$ ,

$$\tilde{\psi}(E^t, E(t)) \geq \tilde{\phi}(E(t)), \quad (2.7)$$

where equality is achieved for the static history  $E^\dagger$ . The first law of thermodynamics is given by

$$\dot{\psi}(t) + D(t) = T(t)\dot{E}(t), \quad D(t) \geq 0, \quad (2.8)$$

where  $D(t) = \tilde{D}(E^t, E(t))$  is the rate of energy dissipation associated with  $\psi(t)$ . The non-negativity of  $D(t)$  is in effect the second law. The integral of (2.8), starting from an undisturbed medium, is given by

$$\psi(t) + \mathfrak{D}(t) = W(t), \quad (2.9)$$

where  $\mathfrak{D}(t)$ , the total dissipation, and  $W(t)$ , the work function, are given by

$$\begin{aligned} \mathfrak{D}(t) &= \int_{-\infty}^t D(u) du = \tilde{\mathfrak{D}}(E^t, E(t)) \geq 0, \\ W(t) &= \int_{-\infty}^t T(u)\dot{E}(u) du = \tilde{W}(E^t, E(t)). \end{aligned} \quad (2.10)$$

It is assumed that both integrals exist.

**2.1. General argument.** The fundamental idea presented here is that a material is uniquely characterized if the rate of dissipation is known for all histories. A detailed method is outlined for linear memory materials in section 6. However, let us at this point give a brief, intuitive sketch of a general version of the argument.

The quantity  $\tilde{D}(E^t, E(t))$  is assumed to be known for all  $(E^t, E(t))$ . Also, we assert as basic axioms that  $W(t)$ , defined on an undisturbed material and the static energy  $\phi(t)$  are both non-negative quantities. They are understood to be specified functions. It follows from (2.7) that  $\psi(t) \geq 0$ . Also,  $\mathfrak{D}(t)$  is given by (2.10)<sub>1</sub>. Then, the free energy is determined by

$$\psi(t) = W(t) - \mathfrak{D}(t), \quad (2.11)$$

and the constitutive relation is (2.6), a result firmly based on the second law [5]. Thus, the material is fully characterized.

This general argument is of course trivial and obvious. What renders the argument given in section 6 more interesting is that a simple useful form of (2.11), derived in [12], is presented.

### 3. LINEAR MEMORY MATERIALS

The constitutive relations with linear memory terms have the equivalent forms

$$\begin{aligned} T(t) &= T_e(t) + \int_0^\infty G'(u) E_r^t(u) du \\ &= T_e(t) + \int_0^\infty \tilde{G}(u) \dot{E}^t(u) du, \\ G'(u) &= \frac{d}{du} G(u), \quad \tilde{G}(u) = G(u) - G_\infty, \\ \dot{E}^t(u) &= \frac{\partial}{\partial t} E^t(u) = -\frac{\partial}{\partial u} E^t(u) = -\frac{\partial}{\partial u} E_r^t(u), \end{aligned} \quad (3.1)$$

where  $T_e(t)$  is the stress function for the equilibrium limit ( $E_r^t(u) = 0$ ,  $u \in \mathbb{R}^+$ ) and the quantity  $G(\cdot) : \mathbb{R}^+ \mapsto \mathbb{R}^+$  is the relaxation function of the material. The assumption is made that

$$\tilde{G}, G' \in L^1(\mathbb{R}^+) \cap L^2(\mathbb{R}^+), \quad (3.2)$$

which will be relevant in the context of taking the Fourier transform of these quantities. The quantity  $T_e(t)$  in (3.1) is given by

$$T_e(t) = \frac{\partial \phi(t)}{\partial E(t)}, \quad (3.3)$$

which is the equilibrium limit of (2.6). For a completely linear material,

$$\tilde{\phi}(E(t)) = \frac{1}{2} G_\infty E^2(t), \quad G_\infty = G(\infty), \quad (3.4)$$

and  $T_e(t)$  is given by the form

$$T_e(t) = G_\infty E(t). \quad (3.5)$$

**3.1. Representation of a free energy and rate of dissipation as quadratic functionals.** For a scalar theory with a linear memory constitutive relation for the stress, the most general form of a free energy is

$$\begin{aligned}\psi(t) &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \mathcal{G}(s, u) E_r^t(u) ds du \\ &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) \tilde{G}(s, u) \dot{E}^t(u) ds du, \\ \mathcal{G}(s, u) &= \frac{\partial^2}{\partial s \partial u} G(s, u) = G_{12}(s, u), \quad \tilde{G}(s, u) = G(s, u) - G_\infty, \\ G(s, \infty) &= G(\infty, s) = G_\infty, \quad s, u \in \mathbb{R}^+.\end{aligned}\tag{3.6}$$

This representation is central to the argument presented here. There is no loss of generality in taking

$$\tilde{G}(s, u) = \tilde{G}(u, s), \quad \mathcal{G}(s, u) = \mathcal{G}(u, s).\tag{3.7}$$

The relaxation function  $G(u)$  is given by

$$G(u) = G(0, u) = G(u, 0) \quad \forall u \in \mathbb{R}^+.\tag{3.8}$$

This relationship is equivalent to the requirement (2.6). Indeed, if we use (3.6)<sub>1</sub> in (2.6), it emerges that  $G'(u) = G_2(0, u) = G_1(u, 0)$ . This is equivalent to (3.8) because of the last two relations of (3.6).

Relation (2.7) requires that the kernels  $\mathcal{G}$  and  $\tilde{G}$  must be such that the integral terms in (3.6)<sub>1,2</sub> are non-negative.

The rate of dissipation can be deduced from (2.8) and (3.6) to be

$$\begin{aligned}D(t) &= -\frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) K(s, u) \dot{E}^t(u) ds du \\ &= -\frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \mathcal{K}(s, u) E_r^t(u) ds du \geq 0,\end{aligned}\tag{3.9}$$

where

$$K(s, u) = G_1(s, u) + G_2(s, u), \quad \mathcal{K}(s, u) = \mathcal{G}_1(s, u) + \mathcal{G}_2(s, u) = K_{12}(s, u).\tag{3.10}$$

As in (3.6)<sub>4</sub>, the subscripts on  $\mathcal{G}$  and  $G$  indicate differentiation with respect to the first or second argument. Recalling (3.7), we see that the quantities  $K$  and  $\mathcal{K}$  can also be taken to be symmetric in their arguments.

There are two equivalent notations, the first being  $\tilde{G}(s, u)$ ,  $K(s, u)$ ,  $\dot{E}^t(s)$  and the second  $\mathcal{G}(s, u)$ ,  $\mathcal{K}(s, u)$ ,  $E_r^t(s)$ . We use both options, with a bias towards the first.

The assumption (see (3.2)) is made that

$$\tilde{G}(\cdot, \cdot), \mathcal{G}(\cdot, \cdot) \in L^1(\mathbb{R}^+ \times \mathbb{R}^+) \cap L^2(\mathbb{R}^+ \times \mathbb{R}^+),\tag{3.11}$$

which will also be relevant in the context of Fourier transforms of these quantities.

**3.2. The work function as a quadratic functional.** This quantity, given by (2.10)<sub>2</sub>, can be put in the following forms ([1], page 153 and earlier references cited

therein):

$$\begin{aligned} W(t) &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) \tilde{G}(|s-u|) \dot{E}^t(u) ds du \\ &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \frac{\partial^2}{\partial s \partial u} G(|s-u|) E_r^t(u) ds du. \end{aligned} \quad (3.12)$$

#### 4. FREQUENCY DOMAIN QUANTITIES

Let  $\Omega$  be the complex  $\omega$  plane and

$$\begin{aligned} \Omega^+ &= \{\omega \in \Omega \mid \text{Im}(\omega) \in \mathbb{R}^+\}, \\ \Omega^{(+)} &= \{\omega \in \Omega \mid \text{Im}(\omega) \in \mathbb{R}^{++}\}. \end{aligned} \quad (4.1)$$

These define the upper half-plane including and excluding the real axis, respectively. Similarly,  $\Omega^-$ ,  $\Omega^{(-)}$  are the lower half-planes including and excluding the real axis, respectively.

**4.1. Relaxation function.** Let us define the quantities

$$\begin{aligned} \tilde{G}_+(\omega) &= \int_0^\infty \tilde{G}(s) e^{-i\omega s} ds = \tilde{G}_c(\omega) - i\tilde{G}_s(\omega), \\ G'_+(\omega) &= \int_0^\infty G'(s) e^{-i\omega s} ds = G'_c(\omega) - iG'_s(\omega). \end{aligned} \quad (4.2)$$

It follows from (3.2) that  $G'_+$  and  $\tilde{G}_+ \in L^2(\mathbb{R})$ . Applying a partial integration in (4.2)<sub>3</sub> yields that

$$G'_c(\omega) = -\tilde{G}_0 + \omega \tilde{G}_s(\omega), \quad G'_s(\omega) = -\omega \tilde{G}_c(\omega). \quad (4.3)$$

The quantities  $\tilde{G}_c(\omega)$  and  $G'_s(\omega)$  obey the equivalent inequalities [7, 1]

$$\tilde{G}_c(\omega) \geq 0, \quad G'_s(\omega) \leq 0 \quad \forall \omega \in \mathbb{R}^{++}, \quad (4.4)$$

which are consequences of the second law. Analyticity and other properties of  $G'_+(\omega)$  are discussed in for example [1], pages 142, 143, 552. The analyticity properties also apply to  $\tilde{G}_+(\omega)$ .

A quantity of significant interest, particularly in the context of the minimum and related free energies, is

$$H(\omega) = -\omega G'_s(\omega) = \omega^2 \tilde{G}_c(\omega) \geq 0, \quad \omega \in \mathbb{R}, \quad (4.5)$$

where the inequality is a consequence of (4.4). One can show that

$$H_\infty = \lim_{\omega \rightarrow \infty} H(\omega) = -G'(0) \geq 0. \quad (4.6)$$

We assume for present purposes that  $G'(0)$  is non-zero so that  $H_\infty$  is a finite, positive number. Then  $H(\omega) \in \mathbb{R}^{++} \forall \omega \in \mathbb{R}$ ,  $\omega \neq 0$ , and can always be expressed as the product of two factors [9, 6, 1]

$$H(\omega) = H_+(\omega) H_-(\omega), \quad (4.7)$$

where  $H_+(\omega)$  has no zeros in  $\Omega^{(-)}$  and is analytic in  $\Omega^-$ . Similarly,  $H_-(\omega)$  is analytic in  $\Omega^+$  with no zeros in  $\Omega^{(+)}$ . We put

$$\begin{aligned} H_\pm(\omega) &= H_\mp(-\omega) = \overline{H_\mp(\omega)}, \\ H(\omega) &= |H_\pm(\omega)|^2, \quad \omega \in \mathbb{R}. \end{aligned} \quad (4.8)$$

The factorization (4.7) is the one relevant to the minimum free energy. For a certain category of material, there is a much broader class of factorizations, where the property that the zeros of  $H_{\pm}(\omega)$  are in  $\Omega^{\pm}$  respectively, need not be true. These generate a range of free energies related to the minimum free energy. In particular, this is true for discrete spectrum materials (introduced in section 5), as described briefly in section 7.

**4.2. Strain history.** We assume that the history of strain  $E^t$  is in  $L^1(\mathbb{R}^+) \cap L^2(\mathbb{R}^+)$ . If the quantity  $E^t(s)$  is taken to be zero for  $s < 0$ , its Fourier transform is given by

$$E_+^t(\omega) = \int_0^{\infty} E^t(s)e^{-i\omega s} ds \in L^2(\mathbb{R}). \quad (4.9)$$

The Fourier transform of  $E_{r+}^t$ , defined by (2.2) and zero for  $s \in \mathbb{R}^{--}$  has the form ([1], page 552)

$$E_{r+}^t(\omega) = E_+^t(\omega) - \frac{E(t)}{i\omega^-} \quad (4.10)$$

The notation  $\omega^{\pm}$  is discussed for example in [1], page 551. We have ([1], page 145)

$$\frac{d}{dt}E_+^t(\omega) = \dot{E}_+^t(\omega) = -i\omega E_+^t(\omega) + E(t) = -i\omega E_{r+}^t(\omega). \quad (4.11)$$

**4.3. Constitutive equations.** Applying Plancherel's theorem to (3.1)<sub>1,2</sub>, and invoking an argument given for example in [1], page 146, we obtain

$$\begin{aligned} T(t) &= T_e(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} [\overline{G'_+}(\omega) + \lambda_1 G'_+(\omega)] E_{r+}^t(\omega) d\omega \\ &= T_e(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} [\overline{\tilde{G}}_+(\omega) + \lambda_2 \tilde{G}_+(\omega)] \dot{E}_+^t(\omega) d\omega, \end{aligned} \quad (4.12)$$

where  $\lambda_1$  and  $\lambda_2$  are arbitrary complex constants. For  $\lambda_1 = -1$  and  $\lambda_2 = 1$ , we have

$$\begin{aligned} T(t) &= T_e(t) + \frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega} E_{r+}^t(\omega) d\omega \\ &= T_e(t) + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} \dot{E}_+^t(\omega) d\omega. \end{aligned} \quad (4.13)$$

Frequency domain representations for the work function (3.12) are given by ([1], page 154)

$$\begin{aligned} W(t) &= \phi(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} \left| \dot{E}_+^t(\omega) \right|^2 d\omega \\ &= \phi(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} H(\omega) \left| E_{r+}^t(\omega) \right|^2 d\omega. \end{aligned} \quad (4.14)$$

Both forms are manifestly non-negative. Note that in both (4.13) and (4.14), one form follows from the other by invoking (4.11).



## 5. DISCRETE SPECTRUM MATERIALS

The forms of the relaxation function and related quantities for discrete spectrum materials are specified in this section. We have

$$\tilde{G}(s) = \sum_{i=1}^n G_i e^{-\alpha_i s}, \quad (5.1)$$

where  $n$  is a positive integer. The inverse decay times  $\alpha_i \in \mathbb{R}^+$ ,  $i = 1, 2, \dots, n$  and the coefficients  $G_i$  are also generally assumed to be positive, this being the simplest way to ensure the condition (4.4), which is clear from (5.2)<sub>2</sub> below. We arrange that  $\alpha_1 < \alpha_2 < \alpha_3 \dots$ . From (4.2)<sub>1</sub>, we have

$$\tilde{G}_+(\omega) = \sum_{i=1}^n \frac{G_i}{\alpha_i + i\omega}, \quad \tilde{G}_c(\omega) = \sum_{i=1}^n \frac{\alpha_i G_i}{\alpha_i^2 + \omega^2}, \quad \tilde{G}_s(\omega) = \omega \sum_{i=1}^n \frac{G_i}{\alpha_i^2 + \omega^2}. \quad (5.2)$$

Relation (4.5) gives

$$H(\omega) = \omega^2 \sum_{i=1}^n \frac{\alpha_i G_i}{\alpha_i^2 + \omega^2} \geq 0, \quad \omega \in \mathbb{R}. \quad (5.3)$$

We will use discrete spectrum materials as realistic but simple examples to illustrate the proposal described in the next section.

## 6. RELATIONS BETWEEN KERNELS

The method developed in [12] for determining free energy functionals with desired non-negativity properties is the basis for the central argument in the present work, according to which a material with memory should be characterized by the kernel of the rate of dissipation,  $K(\cdot, \cdot)$ , defined in (3.10). Using a simple formula, the kernel of a unique free energy,  $\tilde{G}(\cdot, \cdot)$ , with the correct non-negativity property, can then be deduced, from which in turn the relaxation function can be obtained.

It is assumed that, as a separate exercise, the equilibrium free energy, defined by (2.5), has been fully determined. For completely linear materials, as given by (3.4) and (3.5), this amounts to measuring  $G_\infty$ .

Thus, all properties of the material are uniquely defined.

It should be emphasized that the kernel of the rate of dissipation must be used as the fundamental quantity defining the material, not the kernel of the free energy,  $\tilde{G}(\cdot, \cdot)$ , even if this latter quantity has the required non-negative property. Indeed, as emphasized in [12], the kernel  $K(\cdot, \cdot)$  associated with such a choice of  $\tilde{G}(\cdot, \cdot)$  need not have the required non-positivity property.

Two equivalent versions of the argument will now be presented, one in the time domain, the other in the frequency domain.

**6.1. Time domain.** We assume that  $K(s, u)$  in (3.10)<sub>1</sub> is given, so that the rate of dissipation for a given strain history of the material, given by (3.9), is uniquely known. We then have the relation

$$\tilde{G}(s, u) = - \int_0^\infty K(z + s, z + u) dz. \quad (6.1)$$

which is derived in [12], where it is also shown to be equivalent to the linear memory version of (2.11). Multiplying (6.1) by  $\dot{E}^t(s)$  and  $\dot{E}^t(u)$  and integrating, one obtains

$$\psi(t) = \phi(t) - \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) K(z+s, z+u) \dot{E}^t(u) ds du dz, \quad (6.2)$$

which is the uniquely defined free energy functional with the non-negativity property required by (2.7), as shown in [12].

It follows from (6.1) and (3.8) that

$$\tilde{G}(s) = \tilde{G}(s, 0) = - \int_0^\infty K(z+s, z) dz = - \int_0^\infty K(z, z+s) dz. \quad (6.3)$$

This gives the relaxation function, which can then be used in (3.1) to obtain the constitutive equation for stress.

**6.2. Frequency domain.** Relations corresponding to those of subsection 6.1, in the frequency domain, can also be given. We define [12]

$$Z_{+-}(\omega_1, \omega_2) = \int_0^\infty \int_0^\infty Z(s, u) e^{-i\omega_1 s + i\omega_2 u} ds du, \quad (6.4)$$

where  $Z(s, u)$  represents the kernel  $\tilde{G}(s, u)$  or  $K(s, u)$ . The quantity  $Z_{+-}(\omega_1, \omega_2)$  is analytic in the lower half of the  $\omega_1$  complex plane and in the upper half of the  $\omega_2$  plane. Just as the comment after (4.2) applies to the relaxation function, relation (3.11) ensures that  $Z_{+-}(\cdot, \cdot) \in L^2(\mathbb{R}^2)$ .

The frequency domain version of the kernels  $\mathcal{K}(s, u)$  and  $\mathcal{G}(s, u)$  occur in quadratic forms expressed in terms of  $E_{r+}^t(\omega)$  rather than  $\dot{E}_+^t(\omega)$ . We can easily switch to this type of functional by using (4.11). Relations (3.10)<sub>1</sub> and (6.4) yield that

$$i(\omega_1 - \omega_2) \tilde{G}_{+-}(\omega_1, \omega_2) = K_{+-}(\omega_1, \omega_2) + \tilde{G}_+(\omega_1) + \overline{\tilde{G}_+(\omega_2)}, \quad (6.5)$$

where  $\tilde{G}_+(\omega)$  is defined by (4.2)<sub>1</sub>. From (3.8), (4.2)<sub>1</sub> and (6.4), it follows that [12]

$$\tilde{G}_{+-}(\omega_1, \omega_2) \sim \begin{cases} \frac{\tilde{G}_+(\omega_1)}{-i\omega_2} & \text{as } \omega_2 \rightarrow \infty, \\ \frac{\tilde{G}_+(\omega_2)}{i\omega_1} & \text{as } \omega_1 \rightarrow \infty. \end{cases} \quad (6.6)$$

These relations are a means of determining  $\tilde{G}_{+-}(\omega)$  from  $\tilde{G}_{+-}(\omega_1, \omega_2)$  and hence deducing the constitutive relation of the form (4.12)<sub>2</sub>. We can write the frequency domain versions of (3.6)<sub>2</sub> and (3.9)<sub>1</sub> in the forms

$$\begin{aligned} \psi(t) &= \phi(t) + \frac{1}{8\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \overline{\dot{E}_+^t(\omega_1)} \tilde{G}_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2, \\ D(t) &= -\frac{1}{8\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2. \end{aligned} \quad (6.7)$$

As for the time domain expressions, we conclude from (2.7) and (2.8) that the quadratic functional in (6.7)<sub>1</sub> must be non-negative, while that in (6.7)<sub>2</sub> must be non-positive. It is shown in [12], using (6.5) and (6.7)<sub>1</sub>, that

$$\psi(t) = \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2, \quad (6.8)$$

which can be derived also by taking the Fourier transform of (6.2). It is the frequency domain version of latter relation. We have [12]

$$K_{+-}(\omega, \omega) = -2 \frac{H(\omega)}{\omega^2} = -2\tilde{G}_c(\omega), \quad (6.9)$$

where (4.5) has been invoked. This formula provides a way of constructing the constitutive equation as given by (4.13), which is more convenient than (6.6).

Thus, if  $K_{+-}(\omega_1, \omega_2)$  is given for all  $\omega_1$  and  $\omega_2 \in \mathbb{R}$ , the material is completely characterized by (6.8) and (6.9).

**6.3. Example: discrete spectrum materials.** The formulae now presented are closely related to those in [1], page 362; see also [12]. Let the kernel  $K(\cdot, \cdot)$  have the form

$$K(s, u) = - \sum_{i,j=1}^n \Gamma_{ij} e^{-\alpha_i s - \alpha_j u}, \quad (6.10)$$

where the symmetric matrix  $\mathbf{\Gamma}$  with components  $\Gamma_{ij}$ ,  $i, j = 1, 2, \dots, n$  is non-negative. The material is characterized by  $\mathbf{\Gamma}$  and the vector  $\boldsymbol{\alpha}$ , with components  $\alpha_i$ ,  $i = 1, 2, \dots, n$ . These parameters are assumed to be known. Then, from (3.9)<sub>1</sub>,

$$D(t) = \frac{1}{2} \sum_{i,j=1}^n \Gamma_{ij} e_i(t) e_j(t) = \frac{1}{2} \mathbf{e} \cdot \mathbf{\Gamma} \mathbf{e}, \quad (6.11)$$

$$e_i(t) = \dot{E}_+^t(-i\alpha_i), \quad i = 1, 2, \dots, n, \quad \mathbf{e} = (e_1(t), e_2(t), \dots, e_n(t)).$$

The final relation is a definition of the vector quantity  $\mathbf{e}(t)$ . Applying (6.1), we obtain

$$\tilde{G}(s, u) = \sum_{i,j=1}^n \frac{\Gamma_{ij}}{\alpha_i + \alpha_j} e^{-\alpha_i s - \alpha_j u}, \quad (6.12)$$

so that from (3.6)<sub>2</sub>

$$\psi(t) = \phi(t) + \frac{1}{2} \sum_{i,j=1}^n \frac{\Gamma_{ij}}{\alpha_i + \alpha_j} e_i(t) e_j(t) = \phi(t) + \frac{1}{2} \mathbf{e} \cdot \mathbf{C} \mathbf{e}, \quad (6.13)$$

where the matrix  $\mathbf{C}$  has components of the form

$$C_{ij} = \frac{\Gamma_{ij}}{\alpha_i + \alpha_j}, \quad i, j = 1, 2, \dots, n. \quad (6.14)$$

Then the relaxation function is given by

$$\tilde{G}(0, u) = \tilde{G}(u) = \sum_{j=1}^n G_j e^{-\alpha_j u}, \quad G_j = \sum_{i=1}^n \frac{\Gamma_{ij}}{\alpha_i + \alpha_j}, \quad j = 1, \dots, n. \quad (6.15)$$

This formally agrees with (5.1), though it is not clear that all the  $G_j$  are positive. This issue is addressed below.

From (6.4), (6.10) and (5.2)<sub>1</sub>, it follows that

$$\begin{aligned} K_{+-}(\omega_1, \omega_2) &= - \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + i\omega_1)(\alpha_j - i\omega_2)}, \\ \tilde{G}_{+-}(\omega_1, \omega_2) &= \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)(\alpha_i + i\omega_1)(\alpha_j - i\omega_2)}, \\ \tilde{G}_+(\omega) &= \sum_{i=1}^n \frac{G_i}{\alpha_i + i\omega} = \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)(\alpha_i + i\omega_1)}. \end{aligned} \quad (6.16)$$

The formula for  $\tilde{G}_+(\omega)$  also follows from (6.6). Observe that

$$\begin{aligned} K_{+-}(\omega, \omega) &= - \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)} \left\{ \frac{1}{\alpha_i + i\omega} + \frac{1}{\alpha_j - i\omega} \right\} \\ &= - \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)} \left\{ \frac{1}{\alpha_i + i\omega} + \frac{1}{\alpha_i - i\omega} \right\} = - \frac{2H(\omega)}{\omega^2}, \end{aligned} \quad (6.17)$$

by virtue of (6.16)<sub>3,4</sub>. This agrees with (6.9).

Let us return to (6.15) and the issue of the positivity of the  $G_j$ . This is not in itself a requirement. What is important is that  $\tilde{G}_c(\omega)$ , given by (5.2)<sub>2</sub>, be non-negative, which is clear from (4.4). Now, from (6.16)<sub>4</sub>,

$$\begin{aligned} \tilde{G}_c(\omega) &= \sum_{i,j}^n \frac{\alpha_i \Gamma_{ij}}{\alpha_i^2 + \omega^2} = \sum_{i,j}^n \frac{\alpha_j \Gamma_{ij}}{\alpha_j^2 + \omega^2} \\ &= \frac{1}{2} \sum_{i,j}^n \frac{(\omega^2 + \alpha_i \alpha_j) \Gamma_{ij}}{(\alpha_i^2 + \omega^2)(\alpha_j^2 + \omega^2)}. \end{aligned} \quad (6.18)$$

This is the sum of two terms, one proportional to  $\omega^2$  in the numerator, and the other proportional to  $\alpha_i \alpha_j$ . Both of these can be seen to be separately non-negative, on recalling that  $\Gamma$  is a non-negative matrix, so we have the desired property (4.4).

This completes the presentation of the central idea of the present work. The question raised in the next section is not in fact closely related to this core point but does utilize a feature of the above discussion, namely that all discrete spectrum materials can be put in the form (6.10).

## 7. THE COMPLETENESS OF A GENERAL, RELAXATION FUNCTION BASED REPRESENTATION

In this section, we will test the completeness of an earlier formula [8, 10, 1], expressed in terms of a family of free energy and rate of dissipation functionals related to the minimum free energy. These lie on the boundary of  $\mathcal{F}$ , the set defined in section 1.

We briefly recall some results relating to this family of functionals. Their derivations are of course relaxation function based. A linear combination of them produces very general rates of dissipation and free energies. It is of interest to determine whether all members of  $\mathcal{F}$  can be expressed in this way. Thus, we are exploring the completeness of this linear combination.

The initial formulae given here relate to general materials with only isolated singularities. The detailed argument is developed in subsection 7.1 for discrete spectrum materials, where the representation (6.10) is used. However, the conclusion applies to more general materials.

The quantity  $H(\omega)$  is a rational function and has various factorizations other than (4.7), denoted by

$$H(\omega) = H_+^f(\omega)H_-^f(\omega), \quad H_{\pm}^f(\omega) = H_{\mp}^f(-\omega) = \overline{H_{\mp}^f(\omega)}, \quad (7.1)$$

where  $f$  is an identification label distinguishing a particular factorization. The value of this label corresponding to the factorization (4.7) is taken to be  $f = 1$ . All other factorizations are obtained by exchanging the zeros of  $H_+(\omega)$  and  $H_-(\omega)$ , leaving the singularities unchanged. Thus,  $H_-^f(\omega)$  has all its singularities in  $\Omega^{(-)}$ . Each exchange of zeros, starting from the factorization (4.7), can be shown to yield a free energy which is greater than or equal to the previous quantity ([8], [1], page 363). The factorization obtained by interchanging all the zeros yields the maximum free energy. It is less than the work function.

One can show (for example [9, 6, 8, 10], [1], pages 339, 353) that the rate of dissipation associated with  $\psi_f(t)$  is

$$D_f(t) = |K_f(t)|^2, \quad (7.2)$$

where

$$K_f(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega)}{\omega} \dot{E}_+^t(\omega) d\omega = \frac{1}{2\pi} \int_{-\infty}^{\infty} H_-^f(\omega) E_{r+}^t(\omega) d\omega, \quad (7.3)$$

We can write  $D_f(t)$ , given by (7.2), as

$$D_f(t) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} \frac{H_+^f(\omega_1)H_-^f(\omega_2)}{\omega_1\omega_2} \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2. \quad (7.4)$$

Comparing (7.4) and (6.7)<sub>2</sub>, we see that

$$K_{+-}(\omega_1, \omega_2) = -2 \frac{H_+^f(\omega_1)H_-^f(\omega_2)}{\omega_1\omega_2}, \quad (7.5)$$

and, by virtue of (6.8) (see also [10], [1], pages 352),

$$\psi_f(t) = \phi(t) + \frac{i}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} H_+^f(\omega_1) H_-^f(\omega_2) \dot{E}_+^t(\omega_2)}{\omega_1 \omega_2 (\omega_1^+ - \omega_2^-)} d\omega_1 d\omega_2. \quad (7.6)$$

The most general rate of dissipation and free energy arising from these factorizations is given by ([10], [1], page 367)

$$D(t) = \sum_{f=1}^N \lambda_f D_f(t), \quad \psi(t) = \sum_{f=1}^N \lambda_f \psi_f(t), \quad \sum_{f=1}^N \lambda_f = 1, \quad \lambda_f \geq 0. \quad (7.7)$$

We will see in subsection 7.1, using the case of discrete spectrum materials, that the expansion (7.7) is not complete, in the sense that there may be valid rate of dissipation functionals that are not expressible in this form.

**7.1. Explicit forms for discrete spectrum materials.** The quantity  $H(w)$  for discrete spectrum materials, given by (5.3), can be expressed as the ratio of two factorized polynomials, and each set of factors, denoted by  $H_{\pm}^f(w)$  in (7.1), can be determined by inspection ([8], [1], page 365).

Explicit expressions for these can be given as follows. Interchanging a zero means in effect switching a given  $\gamma_i$  to  $-\gamma_i$  in both  $H_+$  and  $H_-$ , given by (4.7). The quantity  $\gamma_1 = 0$  and so cannot be exchanged. Let us introduce an  $n$ -dimensional vector  $\epsilon_i^f$ ,  $i = 1, 2, \dots, n$  where each  $\epsilon_i^f$  can take values  $\pm 1$ . We define  $\rho_i^f = \epsilon_i^f \gamma_i$ , and write

$$\begin{aligned} H_+^f(\omega) &= h_{\infty} \prod_{i=1}^n \left\{ \frac{\omega - i\rho_i^f}{\omega - i\alpha_i} \right\}, \\ H_-^f(\omega) &= h_{\infty} \prod_{i=1}^n \left\{ \frac{\omega + i\rho_i^f}{\omega + i\alpha_i} \right\}. \end{aligned} \quad (7.8)$$

In general, each distinct factorization leads to a different rate of dissipation and free energy functional. Possibly, this may not be true in special cases, but these are not considered here. Therefore, the number of distinct rates of dissipation created by interchanging zeros is  $2^{n-1}$ . Also, the number of terms in  $(7.7)_1$  and the number of parameters  $\lambda_f$  is  $2^{n-1}$ .

The relevant formulae for our purposes given in [8, 3, 1, 12] are now summarized, in terms of  $\dot{E}_+^t(-i\alpha_i)$  rather than  $E_{r+}^t(-i\alpha_i)$ . Equations (7.8) can be written as

$$\begin{aligned} H_-^f(\omega) &= ih_{\infty}\omega \sum_{i=1}^n \frac{R_i^f}{\alpha_i(\alpha_i - i\omega)}, \quad H_+^f(\omega) = \overline{H_-^f}(\omega), \\ R_i^f &= (\rho_i^f - \alpha_i) \prod_{\substack{j=1 \\ j \neq i}}^n \left\{ \frac{\rho_j^f - \alpha_i}{\alpha_j - \alpha_i} \right\}. \end{aligned} \quad (7.9)$$

One can show that

$$K_f(t) = -h_{\infty} \left[ \sum_{i=1}^n \frac{R_i^f e_i(t)}{\alpha_i} \right], \quad (7.10)$$

where the  $e_i(t)$  are defined by (6.11)<sub>3</sub>. From (7.2) and (7.10), we see that

$$D_f(t) = H_{\infty} \left[ \sum_{i=1}^n \frac{R_i^f}{\alpha_i} e_i(t) \right]^2 = H_{\infty} \sum_{i,j=1}^n \frac{R_i^f R_j^f}{\alpha_i \alpha_j} e_i(t) e_j(t). \quad (7.11)$$

Let us assume that the material is fully specified so that the matrix  $\mathbf{\Gamma}$  and the vector  $\boldsymbol{\alpha}$  are known. The parameters  $\rho_j^f$  in the  $R_i^f$  are functions of  $\mathbf{\Gamma}$  and  $\boldsymbol{\alpha}$ , and are also given. The expansion  $(7.7)_1$  is complete, in the sense that any rate of dissipation can be put in this form, if we can always find a set of  $N = 2^{n-1}$  parameters  $\lambda_f$  such that the  $M = 1 + n(n+1)/2$  equations and  $N$  inequalities

$$2H_{\infty} \sum_{f=1}^N \lambda_f \frac{R_i^f R_j^f}{\alpha_i \alpha_j} = \Gamma_{ij}, \quad \sum_{f=1}^N \lambda_f = 1, \quad \lambda_f \geq 0, \quad f = 1, 2, \dots, N, \quad (7.12)$$

have a solution. Otherwise, it is not complete. If  $n \leq 4$  then  $N < M$  and no solutions exists, except in very special cases. Thus, the expansion  $(7.7)_1$  is not complete.

However, for  $n > 5$ , we have  $N > M$  and it is likely that solutions are always possible. This may be true also for  $n = 5$  for which  $N = M$ . Therefore, the problem of incompleteness is a feature only of materials with small  $n$ .

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