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Free Energies for Materials with Memory in Terms of State Functionals

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NEW TRENDS IN FLUID AND SOLID MECHANICAL MODELS

Free energies for materials with memory in terms of state functionals

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Abstract The aim of this work is to determine what free energy functionals are expressible as quadratic forms of the state functional I^t which is discussed in earlier papers. The single integral form is shown to include the functional ψ_F proposed a few years ago, and also a further category of functionals which are easily described but more complicated to construct. These latter examples exist only for certain types of materials. The double integral case is examined in detail, against the background of a new systematic approach developed recently for double integral quadratic forms in terms of strain history, which was used to uncover new free energy functionals. However, while, in principle, the same method should apply to free energies which can be given by quadratic forms in terms of I^t, it emerges that this requirement is very restrictive; indeed, only the minimum free energy can be expressed in such a manner.

Keywords Thermodynamics · Memory effects · Free energy functional · Minimal state functional · Rate of dissipation

1 Introduction

Free energy functionals that are expressible as quadratic forms of the state functional I^t are explored in the present work. The quantity I^t is discussed in [1, 6, 7] and elsewhere. Such free energies have applications in proving results concerning the integro-partial differential equations describing materials with memory. They may also be useful for physical modeling of such materials. However, these applications generally require that the free energy functionals involved have compact, explicit analytic representation.

The single integral form is shown to include the functional ψ_F, proposed some years ago [1, 6]. There is also however a further category of functionals of this kind for materials with non-singleton minimal states. These functionals are easily described but more difficult to construct, since basic inequalities relating to thermodynamics must be explicitly imposed; they are therefore not so useful for practical applications.

The double integral quadratic form is examined in detail. In this context, a recent paper [10] deals with determining new free energies that are quadratic functionals of the history of strain, using a novel approach. This new 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.

In principle, the methods developed in [10] apply to quadratic forms in terms of I^t, and should lead to new

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free energies which can be expressed as such quadratic forms. It emerges however that this is a very restrictive property; indeed, only the minimum free energy is expressible as such a functional.

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, $(***)_5$ refers to the fifth "=" sign, if all the relations are equalities. Relations with "∈" are ignored for this purpose.

2 Quadratic models for free energies

As in [10], we discuss the scalar problem, denoting the independent field variable by $E(t)$, the strain function, and the dependent variable by $T(t)$, the stress function. However, it is fairly straightforward to generalize to tensor fields (for example, [1, 5]) and to certain other theories such as heat flow in rigid bodies or electromagnetic phenomena.

Certain basic formulae from [10] and earlier work are repeated here for convenience. The current value of the strain function is $E(t)$ while the strain history and relative history are given by

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

It is assumed here that

$$\lim_{s\to\infty} E^t(s) = \lim_{u\to-\infty} E(u) = 0, \tag{2.2}$$

which simplifies certain formulae. The state of the material, in the most basic sense, is specified by $(E^t, E(t))$ or $(E^t_r, E(t))$. Another definition of state will be introduced in Sect. 5.1.

Let $T(t)$ be the stress at time t. Then the constitutive relations with linear memory terms have the form

$$\begin{aligned} T(t) &= T_e(t) + \int_0^\infty \widetilde{G}(u)\dot{E}^t(u)du, \quad \widetilde{G}(u) = G(u) - G_\infty, \\ &= T_e(t) + \int_0^\infty G'(u)E^t_r(u)du, \dot{E}^t(u) = \frac{\partial}{\partial t}E^t(u) \\ &= -\frac{\partial}{\partial u}E^t(u) = -\frac{\partial}{\partial u}E^t_r(u), \ddot{E}^t(u) = -\frac{\partial}{\partial u}\dot{E}^t(u), \end{aligned} \tag{2.3}$$

where $T_e(t)$ is the stress function for the equilibrium limit, defined by the condition $E^t(s) = E(t) \ \forall s \in \mathbb{R}^+$, and the quantity $G(\cdot): \mathbb{R}^+ \mapsto \mathbb{R}^+$ is the relaxation function of the material. We define

$$\begin{aligned} &G'(u) = \frac{d}{du}G(u), \quad G_\infty = G(\infty), \quad G_0 = G(0), \\ &\widetilde{G}(0) = G_0 - G_\infty = \widetilde{G}_0. \end{aligned} \tag{2.4}$$

The assumption is made that

$$\widetilde{G}, G' \in L^1(\mathbb{R}^+) \cap \mathrm{L}^2(\mathbb{R}^+). \tag{2.5}$$

Remark 2.1 Various formulae presented here can be expressed either in terms of quantities related to $\widetilde{G}(u)$ and $\dot{E}^t(u)$ or $G'(u)$ and $E^t_r(u)$ ([1, 10] and earlier references). We shall generally use those related to $\widetilde{G}(u)$ and $\dot{E}^t(u)$.

Let us denote a particular free energy at time t by $\psi(t) = \tilde{\psi}(E^t, E(t))$, where $\tilde{\psi}$ is understood to be a functional of E^t and a function of $E(t)$. The Graffi [11] conditions obeyed by any free energy are given as follows:

P1:

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

P2: For any history E^t

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

where $\phi(t)$ is the equilibrium value of the free energy $\psi(t)$, defined as

$$\begin{aligned} &\tilde{\phi}(E(t)) = \phi(t) = \tilde{\psi}(E^t, E(t)), \\ &\text{where} \quad E^t(s) = E(t) \ \ \forall s \in \mathbb{R}^+. \end{aligned} \tag{2.8}$$

Thus, equality in (2.7) is achieved for equilibrium conditions.

P3: It is assumed that ψ is differentiable. For any $(E^t, E(t))$ we have the first law

$$\dot{\psi}(t) + D(t) = T(t)\dot{E}(t), \tag{2.9}$$

where $D(t) \geq 0$ is the rate of dissipation of energy associated with $\psi(t)$.
This non-negativity requirement on $D(t)$ is an expression of the second law.

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Integrating (2.9) over $(-\infty, t]$ yields that

$$\psi(t) + \mathfrak{D}(t) = W(t), \tag{2.10}$$

where

$$W(t) = \int_{-\infty}^{t} T(u)\dot{E}(u)du, \quad \mathfrak{D}(t) = \int_{-\infty}^{t} D(u)du \geq 0. \tag{2.11}$$

We assume that these integrals are finite. The quantity $W(t)$ is the work function, while $\mathfrak{D}(t)$ is the total dissipation resulting from the entire history of deformation of the body.

The function $T_e(t)$ in (2.3) is given by

$$T_e(t) = \frac{\partial\phi(t)}{\partial E(t)}. \tag{2.12}$$

It follows that

$$\dot{\phi}(t) = T_e(t)\dot{E}(t). \tag{2.13}$$

For a scalar theory with a linear memory constitutive relation defining stress, the most general form of a free energy is

$$\psi(t) = \phi(t) + \frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s)\widetilde{G}(s,u)\dot{E}^t(u)dsdu,$$
$$\widetilde{G}(s,u) = G(s,u) - G_\infty. \tag{2.14}$$

There is no loss of generality in taking

$$\widetilde{G}(s,u) = \widetilde{G}(u,s). \tag{2.15}$$

The Graffi condition P2, given by (2.7), requires that the kernel $\widetilde{G}$ must be such that the integral term in (2.14) is non-negative. Various properties of $\widetilde{G}(s,u)$ are given in [10] and earlier references. The relaxation function $G(u)$ introduced in (2.3) is related to $G(s,u)$ by

$$G(u) = G(0,u) = G(u,0) \quad \forall u \in \mathbb{R}^+. \tag{2.16}$$

Note that, with the aid of (2.4), we have

$$G(0) = G(0,0) = G_0. \tag{2.17}$$

The rate of dissipation can be deduced from (2.9) and (2.3) to be

$$D(t) = -\frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s)K(s,u)\dot{E}^t(u)dsdu, \tag{2.18}$$

where

$$K(s,u) = G_1(s,u) + G_2(s,u). \tag{2.19}$$

The subscripts 1, 2 indicate differentiation with respect to the first and second arguments. The quantity G must be such that the integral in (2.18) is non-positive, as required by P3 of the Graffi conditions. The quantity K can also be taken to be symmetric in its arguments, *i.e.*

$$K(s,u) = K(u,s). \tag{2.20}$$

Seeking to express $\mathfrak{D}(t)$, given by $(2.11)_2$, as a general quadratic functional form similar to those in (2.14) or (2.18), we put

$$\mathfrak{D}(t) = \frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s)Q(s,u)\dot{E}^t(u)dsdu. \tag{2.21}$$

2.1 The work function

This quantity, given by $(2.11)_1$, can be put in the form ([1, 10], p 153 and earlier references cited therein):

$$W(t) = \phi(t) + \frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s)\widetilde{G}(|s-u|)\dot{E}^t(u)duds. \tag{2.22}$$

We see that it has the form (2.14) where

$$\widetilde{G}(s,u) = \widetilde{G}(|s-u|). \tag{2.23}$$

Remark 2.2 The quantity $W(t)$ can be regarded as a free energy, but with zero total dissipation, which is clear from (2.10). Because of the vanishing dissipation, it must be the maximum free energy associated with the material or greater than this quantity, an observation which follows from (2.10).

Thus, we have in general the requirement that

$$\psi(t) \leq W(t). \tag{2.24}$$

It follows from (2.10) that $Q(s,u)$ in (2.21) is given by

$$Q(s,u) = \widetilde{G}(|s-u|) - \widetilde{G}(s,u), \tag{2.25}$$

so that

$$Q(s,0) = Q(0,u) = 0, \quad \forall s,u \in \mathbb{R}^+. \tag{2.26}$$

Remark 2.3 The integral term in (2.14) and (2.21) are in general positive-definite quadratic forms, in the

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sense that they vanish only if $\dot{E}^t(u) = 0,\ u \in \mathbb{R}^+$, while $D(t)$, given by (2.18), may be positive semi-definite, so that it can vanish for non-zero histories.

3 Frequency domain quantities

Let Ω be the complex ω plane and

$$\Omega^+ = \{\omega \in \Omega \mid Im(\omega) \in \mathbb{R}^+\},$$
$$\Omega^{(+)} = \{\omega \in \Omega \mid Im(\omega) \in \mathbb{R}^{++}\}.$$

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

Remark 3.1 Throughout this work, a subscript "+" attached to any quantity defined on Ω will imply that it is analytic on Ω^-, with all its singularities in $\Omega^{(+)}$. Similarly, a subscript "−" will indicate that it is analytic on Ω^+, with all its singularities in $\Omega^{(-)}$.

The notation for and properties of Fourier transformed quantities is specified in [1, 10] and earlier references. It is assumed that all frequency domain quantities of interest are analytic on an open set including the real axis. The functions and relations

$$\widetilde{G}_+(\omega) = \int_0^\infty \widetilde{G}(s)e^{-i\omega s}ds = \widetilde{G}_c(\omega) - i\widetilde{G}_s(\omega),$$
$$G'_+(\omega) = \int_0^\infty G'(s)e^{-i\omega s}ds = G'_c(\omega) - iG'_s(\omega)$$
$$= -\widetilde{G}_0 + i\omega\widetilde{G}_+(\omega) \tag{3.2}$$

will be required, where the quantities $\widetilde{G}_c(\omega)$, $G'_c(\omega)$ and $\widetilde{G}_s(\omega)$, $G'_s(\omega)$ are the cosine and sine transforms of $\widetilde{G}(s)$, $G'(s)$, respectively; the former quantities are even functions of ω while the latter are odd functions. It follows from (2.5) that $\widetilde{G}_+(\omega), G'_+(\omega) \in L^2(\mathbb{R})$. The quantities $\widetilde{G}_+(\omega)$ and $G'_+(\omega)$ are analytic in Ω^-. Because $\widetilde{G}$ is real, we have

$$\overline{\widetilde{G}_+(\omega)} = \widetilde{G}_+(-\overline{\omega}). \tag{3.3}$$

This constraint means that the singularities are symmetric under reflection in the positive imaginary axis. A similar relation applies to $G'_+(\omega)$. Also, we have

$$G''_+(\omega) = \int_0^\infty G''(s)e^{-i\omega s}ds = -G'(0) + i\omega G'_+(\omega). \tag{3.4}$$

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

$$(\omega) = \omega^2 \widetilde{G}_c(\omega) = -\omega G'_s(\omega) = -G''_c(\omega)$$
$$- G'(0) \geq 0, \quad \omega \in \mathbb{R}, \tag{3.5}$$

where the inequality is an expression of the second law ([1], p 159 and earlier references). The quantity $H(\omega)$ goes to zero quadratically at the origin since $H(\omega)/\omega^2$ tends to a finite, non-zero quantity $\widetilde{G}_c(0)$, as ω tends to zero. One can show that

$$H_\infty = \lim_{\omega \to \infty} H(\omega) = -G'(0) \geq 0. \tag{3.6}$$

We assume for present purposes that $G'(0)$ is non-zero so that H_∞ is a finite, positive number. Then $H(\omega) \in \mathbb{R}^{++}\ \forall\, \omega \in \mathbb{R},\ \omega \neq 0$.

If $G(s)$, $s \in \mathbb{R}^+$, is extended to the even function $G(|s|)$ on $\mathbb{R}$, then $dG(|s|)/ds$ is an odd function with Fourier transform ([1], p 144)

$$G'_F(\omega) = -2iG'_s(\omega) = \frac{2i}{\omega}H(\omega). \tag{3.7}$$

The non-negative quantity $H(\omega)$ can always be expressed as the product of two factors [8]

$$H(\omega) = H_+(\omega)H_-(\omega), \tag{3.8}$$

where $H_+(\omega)$ has no singularities or zeros in $\Omega^{(-)}$ and is thus analytic in Ω^-. Similarly, $H_-(\omega)$ is analytic in Ω^+ with no zeros in $\Omega^{(+)}$. We put [1, 8]

$$H_\pm(\omega) = H_\mp(-\omega) = \overline{H_\mp}(\omega),$$
$$H(\omega) = |H_\pm(\omega)|^2, \quad \omega \in \mathbb{R}. \tag{3.9}$$

The factorization (3.8) is the one relevant to the minimum free energy. For materials with only isolated singularities, we shall require 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 [1, 7, 9], as discussed briefly in Sect. 4.

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The Fourier transform of $E^t(s)$, $E^t_r(s)$, given by (2.1) for $s \in \mathbb{R}^+$, are defined for example in [1, 10] and denoted by $E^t_+(\omega)$, $E^t_{r+}(\omega)$. These have the same analyticity properties as $\widetilde{G}_+(\omega)$. However, $E^t_r(s)$ does not have the property (2.5), so that $E^t_{r+}(\omega)$ must be defined with care. For a constant history, $E^t(s) = E(t)$, $s \in \mathbb{R}^+$, we have ([1], p 551)

$$E^t_+(\omega) = \frac{E(t)}{i\omega^-}, \tag{3.10}$$

where the notation ω^- (and ω^+) is defined in [1, 10] and earlier work. Briefly, $x^\pm = x \pm i\alpha$, respectively, where $\alpha \to 0^+$ after integrations are carried out. Thus, we have

$$E^t_{r+}(\omega) = E^t_+(\omega) - \frac{E(t)}{i\omega^-}. \tag{3.11}$$

Also ([1], p 145),

$$\frac{d}{dt}E^t_+(\omega) = \dot{E}^t_+(\omega) = -i\omega E^t_+(\omega) + E(t) = -i\omega E^t_{r+}(\omega), \tag{3.12}$$

and

$$\frac{d}{dt}\dot{E}^t_+(\omega) = -i\omega \dot{E}^t_+(\omega) + \dot{E}(t),$$
$$\frac{d}{dt}E^t_{r+}(\omega) = \dot{E}^t_{r+}(\omega) = -i\omega E^t_{r+}(\omega) - \frac{\dot{E}(t)}{i\omega^-}.$$

For large ω,

$$E^t_+(\omega) \sim \frac{E(t)}{i\omega}, \quad E^t_{r+}(\omega) \sim \frac{A(t)}{\omega^2}, \tag{3.14}$$

where $A(t)$ is independent of ω. Also, from (3.12),

$$\dot{E}^t_+(\omega) \sim \frac{A(t)}{i\omega}, \tag{3.15}$$

for large ω. Relation (3.12) is convenient for converting formulae from those in terms of $E^t_{r+}(\omega)$ to equivalent expressions in terms of $\dot{E}^t_+(\omega)$ or vice versa.

Applying Parseval's formula to $(2.3)_1$, we obtain

$$T(t) = T_e(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty} \overline{\widetilde{G}_+}(\omega) E^t_+(\omega)\, d\omega. \tag{3.16}$$

There is a non-uniqueness in this form allowing us to write it as [1, 10]

$$T(t) = T_e(t) + \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2}\dot{E}^t_+(\omega) d\omega. \tag{3.17}$$

More detail is included on this argument in (5.38)–(5.40) below.

We shall be using the Plemelj formulae on the real axis ([1], p 542) several times in this work, in relation to frequency dependent quantities. These are given as follows. Let

$$F(z) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{f(u)}{u-z}du, \quad z \in \Omega \backslash \mathbb{R}, \tag{3.18}$$

where $f(u)$ is any Hölder continuous function. For $z \in \Omega^{(+)}$, the function $F(z)$ is analytic in $\Omega^{(+)}$, while for $z \in \Omega^{(-)}$, it is analytic in $\Omega^{(-)}$. Let $z = x + i\alpha$, $\alpha > 0$ where α approaches zero. Then, we write (3.18) as (recall Remark 3.1)

$$F_-(x) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{f(u)}{u-x^+}du = \frac{1}{2}f(x) + \frac{1}{2\pi i}P\int_{-\infty}^{\infty} \frac{f(u)}{u-x}du, \tag{3.19}$$

where the symbol "P" indicates a principal value integral. Similarly,

$$F_+(x) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{f(u)}{u-x^-}du = -\frac{1}{2}f(x) + \frac{1}{2\pi i}P\int_{-\infty}^{\infty} \frac{f(u)}{u-x}du. \tag{3.20}$$

4 The minimum and related free energies

It is shown in [7, 9] that, for materials with only isolated singularities, the quantity $H(\omega)$ is a rational function and has many factorizations other than (3.8), denoted by

$$H(\omega) = H^f_+(\omega)H^f_-(\omega),$$
$$H^f_\pm(\omega) = H^f_\mp(-\omega) = \overline{H^f_\mp}(\omega), \tag{4.1}$$

where f is an identification label distinguishing a particular factorization. These are obtained by exchanging the zeros of $H_+(\omega)$ and $H_-(\omega)$, leaving the singularities unchanged.

Each factorization yields a (usually) different free energy of the form

$$\psi_f(t) = \phi(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty} \left|p_-^{ft}(\omega)\right|^2 d\omega, \tag{4.2}$$

where, recalling (3.12),

$$\begin{aligned} P^{ft}(\omega) &= i\frac{H_-^f(\omega)}{\omega}\dot{E}_+^t(\omega) = H_-^f(\omega)E_{r+}^t(\omega) \\ &= p_-^{ft}(\omega) - p_+^{ft}(\omega), \\ p_\pm^{ft}(\omega) &= \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{P^{ft}(\omega')}{\omega' - \omega^\mp}d\omega'. \end{aligned} \tag{4.3}$$

The quantity p_-^{ft} is analytic on Ω^+ while p_+^{ft} is analytic on Ω^- [1]. Note that (4.3) involves the use of the Plemelj formulae, as given by (3.19) and (3.20). The total dissipation is given by

$$\mathfrak{D}_f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \left|p_+^{ft}(\omega)\right|^2 d\omega. \tag{4.4}$$

Defining

$$\begin{aligned} K_f(t) &= -\frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{H_-^f(\omega)}{\omega}\dot{E}_+^t(\omega)d\omega \\ &= \lim_{\omega\to\infty}[-i\omega p_-^{ft}(\omega)], \end{aligned} \tag{4.5}$$

we can write the associated rate of dissipation in the form

$$D_f(t) = \left|K_f(t)\right|^2. \tag{4.6}$$

These formulae apply in particular to the case where no exchange of zeros takes place, which is denoted by $f = 1$. In this case, the formulae in fact apply to all materials, not just those characterized by isolated singularities.

We can write $\psi_f(t)$ in the form [1, 8–10]

$$\psi_f(t) = \phi(t) + \frac{i}{4\pi^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t}(\omega_1)H_+^f(\omega_1)H_-^f(\omega_2)\dot{E}_+^t(\omega_2)}{\omega_1\omega_2(\omega_1^+ - \omega_2^-)}d\omega_1 d\omega_2. \tag{4.7}$$

The notation in the denominator [1, 10] indicates that if, for example, the ω_1 integration is carried out first, then $\omega_1^+ - \omega_2^-$ becomes $\omega_1 - \omega_2^-$. Also, the total dissipation (see (4.4)) can be shown, by similar manipulations, to have the form

$$\mathfrak{D}_f(t) = -\frac{i}{4\pi^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t}(\omega_1)H_+^f(\omega_1)H_-^f(\omega_2)\dot{E}_+^t(\omega_2)}{\omega_1\omega_2(\omega_1^- - \omega_2^+)}d\omega_1 d\omega_2, \tag{4.8}$$

while $D_f(t)$, given by (4.6), can be expressed as

$$D_f(t) = \frac{1}{4\pi^2}\int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t}(\omega_1)H_+^f(\omega_1)H_-^f(\omega_2)\dot{E}_+^t(\omega_2)}{\omega_1\omega_2}d\omega_1 d\omega_2. \tag{4.9}$$

The factorization $f = 1$, given by (3.8), yields the minimum free energy $\psi_m(t)$. Each exchange of zeros, starting from these factors, yields a free energy which is greater than or equal to the previous quantity. The maximum free energy, denoted by $\psi_M(t)$, is obtained by interchanging all the zeros, which produces a factorization labeled $f = N$. The quantity $\psi_M(t)$ is less than the work function [1, 10].

The most general free energy and rate of dissipation arising from these factorizations is given by

$$\begin{aligned} &\psi(t) = \sum_{f=1}^{N}\lambda_f\psi_f(t), \quad D(t) = \sum_{f=1}^{N}\lambda_f D_f(t), \\ &\sum_{f=1}^{N}\lambda_f = 1, \quad \lambda_f \geq 0. \end{aligned} \tag{4.10}$$

A particular case of this linear form is the physical free energy, proposed in [9].

4.1 Discrete spectrum materials

Consider a material with relaxation function of the form

$$\widetilde{G}(s) = \sum_{i=1}^{n} G_i e^{-\alpha_i s}, \tag{4.11}$$

where n is a positive integer. The inverse decay times $\alpha_i \in \mathbb{R}^{++}$, $i = 1, 2, \ldots, n$ and the coefficients G_i are assumed to be positive. We arrange that

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$\alpha_1 < \alpha_2 < \alpha_3 \ldots$. These are discrete spectrum materials which will be used in later discussions.

From (3.2)$_{1,2}$, we have

$$\widetilde{G}_+(\omega) = \sum_{i=1}^{n} \frac{G_i}{\alpha_i + i\omega}, \quad \widetilde{G}_c(\omega) = \sum_{i=1}^{n} \frac{\alpha_i G_i}{\alpha_i^2 + \omega^2},$$
$$\widetilde{G}_s(\omega) = \omega \sum_{i=1}^{n} \frac{G_i}{\alpha_i^2 + \omega^2}, \tag{4.12}$$

so that $\widetilde{G}_+(\omega)$ consists of a sum of simple pole terms on the positive imaginary axis. From (2.3)$_1$ and (4.11), we have that

$$T(t) = T_e(t) + \sum_{i=1}^{n} G_i \dot{E}_+^t(-i\alpha_i). \tag{4.13}$$

Relations (3.5) and (4.12)$_2$ give

$$H(\omega) = \omega^2 \sum_{i=1}^{n} \frac{\alpha_i G_i}{\alpha_i^2 + \omega^2} = H_\infty - \sum_{i=1}^{n} \frac{\alpha_i^3 G_i}{\alpha_i^2 + \omega^2} \geq 0,$$
$$H_\infty = \sum_{i=1}^{n} \alpha_i G_i. \tag{4.14}$$

This quantity can be expressed in the form [8]

$$H(\omega) = H_\infty \prod_{i=1}^{n} \left\{ \frac{\gamma_i^2 + \omega^2}{\alpha_i^2 + \omega^2} \right\}, \tag{4.15}$$

where the γ_i^2 are the zeros of $f(z) = H(\omega)$, $z = -\omega^2$, and obey the relations

$$\gamma_1 = 0, \quad \alpha_1^2 < \gamma_2^2 < \alpha_2^2 < \gamma_3^2 \ldots \tag{4.16}$$

Observe that

$$G_i = \frac{2i}{\alpha_i^2} \lim_{\omega \to -i\alpha_i} (\omega + i\alpha_i) H(\omega)$$
$$= -\frac{2i}{\alpha_i^2} \lim_{\omega \to i\alpha_i} (\omega - i\alpha_i) H(\omega). \tag{4.17}$$

To obtain the minimum free energy for discrete spectrum materials, one chooses the factorization of (4.15) given by

$$H_+(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega - i\gamma_i}{\omega - i\alpha_i} \right\}, \quad h_\infty = [H_\infty]^{1/2},$$
$$H_-(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega + i\gamma_i}{\omega + i\alpha_i} \right\} = \overline{H_+(\omega)}. \tag{4.18}$$

Equations (4.18) can be written as [1, 2]

$$H_-(\omega) = h_\infty \left[1 + i \sum_{i=1}^{n} \frac{U_i}{\omega + i\alpha_i} \right] = -h_\infty \omega \sum_{i=1}^{n} \frac{U_i}{\alpha_i(\omega + i\alpha_i)},$$
$$U_i = (\gamma_i - \alpha_i) \prod_{\substack{j=1 \\ j \neq i}}^{n} \left\{ \frac{\gamma_j - \alpha_i}{\alpha_j - \alpha_i} \right\}, \qquad \sum_{i=1}^{n} \frac{U_i}{\alpha_i} = -1. \tag{4.19}$$

For discrete spectrum materials, the interchange of zeros referred to after (4.1) means switching a given γ_i to $-\gamma_i$ in both $H_+(\omega)$ and $H_-(\omega)$. Let us introduce an n-dimensional vector with components ϵ_i^f, $i = 1, 2, \ldots, n$ where each ϵ_i^f can take values ± 1. We define $\rho_i^f = \epsilon_i^f \gamma_i$, and write

$$H_+^f(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega - i\rho_i^f}{\omega - i\alpha_i} \right\}, \quad H_-^f(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega + i\rho_i^f}{\omega + i\alpha_i} \right\}. \tag{4.20}$$

The case where all the zeros are interchanged [1, 6, 7, 9] is labeled $f = N$. The resulting factors are given by

$$H_+^N(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega + i\gamma_i}{\omega - i\alpha_i} \right\}, \quad H_-^N(\omega) = h_\infty \prod_{i=1}^{n} \left\{ \frac{\omega - i\gamma_i}{\omega + i\alpha_i} \right\}. \tag{4.21}$$

5 The functional I^t

5.1 Minimal states

As noted after (2.2), a viscoelastic state is defined in general by the history and current value of strain $(E^t, E(t))$. The concept of a minimal state, defined in [7] and based on the work of Noll [13] (see also for example [1, 3–5, 12]), can be expressed as follows: two viscoelastic states $(E_1^t, E_1(t))$, $(E_2^t, E_2(t))$ are equivalent or in the same equivalence class or minimal state if

$$E_1(t) = E_2(t), \int_0^\infty G'(s+\tau)\left[E_1^t(s) - E_2^t(s)\right] ds$$
$$= I^t(\tau, E_1^t) - I^t(\tau, E_2^t) = 0 \ \forall \tau \geq 0,$$
$$I^t(\tau, E^t) = \int_0^\infty G'(s+\tau) E_r^t(s) ds = \int_0^\infty \widetilde{G}(s+\tau) \dot{E}^t(s) ds$$
$$= I^t(\tau). \tag{5.1}$$

The abbreviated notation $I^t(\tau)$ will be used henceforth. Note the property

$$\lim_{\tau\to\infty} I^t(\tau) = 0. \tag{5.2}$$

It follows from $(2.3)_1$ and (5.1) that

$$I^t(0) = T(t) - T_e(t). \tag{5.3}$$

A functional of $(E^t, E(t))$ which yields the same value for all members of the same minimal state is referred to as a FMS or functional of the minimal state, or a minimal state variable. The quantity $I^t(\tau)$ is a FMS, in fact, the defining example of a FMS.

Remark 5.1 A distinction between materials [1] is that for certain relaxation functions, namely those with only isolated singularities (in the frequency domain), the minimal states are non-singleton, while if some branch cuts are present in the relaxation function, the material has only singleton minimal states. For relaxation functions with only isolated singularities, there is a maximum free energy that is less than the work function $W(t)$ and also a range of related intermediate free energies, as noted in Sect. 4.

On the other hand, if branch cuts are present, the maximum free energy is $W(t)$ and there are no intermediate free energies of type $\psi_f(t)$.

Remark 5.2 There will be some later contexts where we confine the discussion to materials with only isolated singularities, for reasons connected with the properties noted in Remark 5.1. Treating the general case of such materials is algebraically complicated [1, 9], because any given singularity or zero may be of higher order. We simplify the treatment, while maintaining the essential content, by separating higher order poles or zeros into simple poles or zeros. A further simplification will be made, which also retains most essential properties,[1] by taking all the singularities and zeros on the imaginary axis. This means, in effect, that the material is a discrete spectrum material, as defined in Sect. 4.1.

[1] There is a noteworthy difference between the general case where singularities may be off the imaginary axis and discrete spectrum materials, namely that in the latter case, the relaxation function decays monotonically, while in the former case, the possibility exists of oscillatory decay.

Thus, we will use discrete spectrum materials as simple but realistic proxies for more general materials with only isolated singularities.

The quantities $p_-^{ft}(\omega)$, defined by (4.3), are FMSs; in particular, $p_-^t(\omega)$ corresponding to the minimum free energy for general materials ([1], p 253). The functionals $p_+^{ft}(\omega)$ do not have this property, by virtue of $(4.3)_2$.

Let us characterize minimal states for discrete spectrum materials in the following simple manner. Consider two states $(E_1^t, E_1(t))$ and $(E_2^t, E_2(t))$ obeying conditions (5.1), so that they are equivalent. We define the difference between these states as $(E_d^t, E_d(t))$ where

$$\begin{aligned} &E_d^t(s) = E_1^t(s) - E_2^t(s) \quad \forall s \in R^+, \\ &E_d(t) = E_1(t) - E_2(t). \end{aligned} \tag{5.4}$$

The conditions (5.1) holds for all $\tau \geq 0$ if and only if

$$E_d(t) = 0, \quad \int_0^\infty e^{-\alpha_i s} E_d^t(s) ds = E_{d+}^t(-i\alpha_i) = 0,$$
$$i = 1, 2, \ldots, n.$$

Remark 5.3 Therefore, for a given discrete spectrum material, the property that two histories are equivalent, or in the same minimal state, is determined by $(5.5)_1$ and by the values of those histories in the frequency domain, at $\omega = -i\alpha_i$, $i = 1, 2, \ldots, n$. This is a special case of the general requirement given in [1], p 359.

Thus, if a quantity depends on the strain history only through the values $E_+^t(-i\alpha_i)$ or $E_{r+}^t(-i\alpha_i)$ or (see (3.12)) $\dot{E}_+^t(-i\alpha_i)$, for $i = 1, 2, \ldots, n$, this quantity is a FMS.

For discrete spectrum materials,

$$I^t(\tau) = \sum_{i=1}^n G_i \dot{E}_+^t(-i\alpha_i) e^{-\alpha_i \tau}, \tag{5.6}$$

which is an example of the property described in Remark 5.3. The property that $p_-^{ft}(\omega)$ is a FMS can be perceived for discrete spectrum materials by completing the contour in $(4.3)_4$ on $\Omega^{(-)}$.

We now present a more general characterization of minimal states, which leads to results consistent with (5.5). The condition that minimal states are non-singleton is that the integral equation

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$$\int_0^\infty G'(s+\tau)E_d^t(s)ds = 0, \quad \tau \in \mathbb{R}^+, \tag{5.7}$$

for $E_d^t(s) = E_1^t(s) - E_2^t(s)$ in (5.1), has non-zero solutions. The other requirement $(5.1)_1$ will be enforced below by (5.17). Putting $E_d^t(s) = 0,\ s \in \mathbb{R}^-$ and $\tau = -u$, we can write (5.7) as ([1], p 341)

$$\int_{-\infty}^\infty \frac{\partial}{\partial u} G(|u-s|)E_d^t(s)ds = 0, \quad u \in \mathbb{R}^-. \tag{5.8}$$

This is a Wiener–Hopf equation, which can be solved by a standard technique. We put

$$\int_{-\infty}^\infty \frac{\partial}{\partial u} G(|u-s|)E_d^t(s)ds = \begin{cases} J(u), & u \in \mathbb{R}^{++} \\ 0, & u \in \mathbb{R}^- \end{cases}, \tag{5.9}$$

where $J(u)$ is a quantity to be determined. Taking the Fourier transform of both sides, we obtain, with the aid of the convolution theorem and (3.7),

$$\frac{2i}{\omega} H(\omega)E_{d+}^t(\omega) = J_+(\omega). \tag{5.10}$$

Using (4.1) and (4.3), we can write (5.10) in the form

$$\frac{2i}{\omega}\left\{ H_+^f(\omega)\left[p_{d-}^{ft}(\omega) - p_{d+}^{ft}(\omega)\right]\right\} = J_+(\omega), \tag{5.11}$$

where the subscript d implies that E_{d+}^t is used in (4.3). The value of the superscript f will be assigned below. Because $p_-^{ft}(\omega)$ is a FMS, we have

$$p_{d-}^{ft}(\omega) = 0. \tag{5.12}$$

It then follows from (5.11) that

$$p_{d+}^{ft}(\omega) = -\frac{\omega}{2i}\frac{J_+(\omega)}{H_+^f(\omega)}. \tag{5.13}$$

Using (5.13) in (5.10), we obtain

$$H(\omega)E_{d+}^t(\omega) = -H_+^f(\omega)p_{d+}^{ft}(\omega), \tag{5.14}$$

or

$$E_{d+}^t(\omega) = -\frac{p_{d+}^{ft}(\omega)}{H_-^f(\omega)}. \tag{5.15}$$

This quantity must be analytic on Ω^-, so that all the zeros of $H_\pm(\omega)$ must have been interchanged. This is the case where $f = N$ and the resulting factors are those given by (4.21), which yield the maximum free energy $\psi_M(t)$, introduced after (4.9).

Thus, if we can find a quantity $E_{d+}^t(\omega)$ which satisfies (5.12), it satisfies (5.14) and (5.15) by virtue of $(4.3)_3$, applied to this history difference. Relation (5.14) is equivalent to (5.10), with $J_+(\omega)$ determined by (5.13). Therefore, a solution to (5.9) or (5.8) is provided by any choice of $E_d^t(s)$ where the corresponding $E_{d+}^t(\omega)$ satisfies (5.12). Now, from $(4.3)_4$,

$$p_{d-}^{Nt}(\omega) = \frac{1}{2\pi i}\int_{-\infty}^\infty \frac{H_-^N(\omega')E_{d+}^t(\omega')}{\omega' - \omega^+} d\omega' = 0. \tag{5.16}$$

If there are non-isolated singularities in the material, we know (remark 5.1) that the only solution is the trivial one, $E_{d+}^t(\omega) = 0$. Thus, we can focus on the case of a material with only isolated singularities. The simplifying assumptions of Remark 5.2 will be adopted so that we are dealing with discrete spectrum materials. Then, $H_\pm^f(\omega)$ are given by (4.20).

The simplifying assumption will now be made that $E_{d+}^t(\omega)$ is a rational function. More generally, it could also have branch cuts in $\Omega^{(+)}$.

At large ω, we must have

$$E_{d+}^t(\omega) \sim \frac{1}{\omega^2}, \tag{5.17}$$

by virtue of (3.14) and $(5.1)_1$. If the zeros of $E_{d+}^t(\omega)$ cancel the poles in $H_-^N(\omega)$, given by (4.21), then, by taking the contour around $\Omega^{(-)}$, we see that (5.16) is obeyed. Thus, non-trivial solutions to (5.8) or (5.10) are given by

$$E_{d+}^t(\omega) = \frac{E_0(t)}{\omega - i\chi_0}\prod_{j=1}^n \left\{\frac{\omega + i\alpha_j}{\omega - i\chi_j}\right\}\frac{1}{\omega - i\chi_{n+1}}, \tag{5.18}$$

where the constants $\chi_i,\ i = 0, 1, \ldots, n+1$ indicate the positions of singularities on the imaginary axis in $\Omega^{(+)}$. These are arbitrary positive quantities. The factor $E_0(t)$, which determines the time dependence of $E_{d+}^t(\omega)$, is also arbitrary. Note that

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(5.18) obeys the constraints (5.5). We can write it in the form

$$E^t_{d+}(\omega) = -iE_0(t)\sum_{i=0}^{n+1}\frac{A_i}{\omega - i\chi_i},$$
$$A_i = \frac{\chi_i+\alpha_i}{\chi_i-\chi_0}\prod_{\substack{j=1\\ j\neq i}}^{n}\left\{\frac{\chi_i+\alpha_j}{\chi_i-\chi_j}\right\}\frac{1}{\chi_i-\chi_{n+1}},$$
$$i = 1,2,\ldots,n,$$
$$A_0 = \prod_{j=1}^{n}\left\{\frac{\chi_0+\alpha_j}{\chi_0-\chi_j}\right\}\frac{1}{\chi_0-\chi_{n+1}},$$
$$A_{n+1} = \frac{1}{\chi_{n+1}-\chi_0}\prod_{j=1}^{n}\left\{\frac{\chi_{n+1}+\alpha_j}{\chi_{n+1}-\chi_j}\right\}, \tag{5.19}$$

where, to satisfy (5.17), we must have

$$\sum_{i=0}^{n+1} A_i = 0. \tag{5.20}$$

Taking the inverse transform of $(5.19)_1$, we obtain that

$$\begin{aligned} E^t_d(s) &= E_0(t)\sum_{i=0}^{n+1}A_i e^{-\chi_i s} \\ &= E^t_d(\chi_j, j=0,1,\ldots,n+1; s). \end{aligned} \tag{5.21}$$

A given history $E^t_1(s)$ belongs to the minimal state with members

$$\begin{aligned} E^t(\chi_j, j=0,1,\ldots,n+1; s) &= E^t_1(s) \\ &+ E^t_d(\chi_j, j=0,1,\ldots,n+1; s), \end{aligned} \tag{5.22}$$

where the parameters χ_j may take any positive value.

If (5.7) is true for $\widetilde{G}$ given by (4.11), we must have

$$\sum_{j=0}^{n+1}\frac{A_j}{\chi_j+\alpha_i} = 0, \quad i = 1,2\ldots,n, \tag{5.23}$$

which is simply a statement that $E^t_{d+}(\omega)$, given by $(5.19)_1$, vanishes at ω equal to each $-i\alpha_i$.

If $E_0(t)$ in (5.18) were replaced by $E_0(\omega,t)$, where $\lim_{\omega\to\infty}E_0(\omega,t)$ is a non-zero finite constant, and the singularities of this quantity consists of branch cuts in $\Omega^{(+)}$, then the resulting $E^t_{d+}(\omega)$ would be equally satisfactory, except that the simple relation (5.21) would not hold.

5.2 Free energies that are FMSs, as quadratic forms of histories for discrete spectrum materials

We now briefly describe a general form of free energies that are FMSs for discrete spectrum materials ([1] and references therein). Let us define a vector $\mathbf{e}$ in $\mathbb{R}^n$ with components

$$\begin{aligned} e_i(t) &= E(t) - \alpha_i E^t_+(-i\alpha_i) = \frac{d}{dt}E^t_+(-i\alpha_i) \\ &= \dot{E}^t_+(-i\alpha_i) = -\alpha_i E^t_{r+}(-i\alpha_i), \quad i = 1,2,\ldots,n, \end{aligned} \tag{5.24}$$

where (3.12) has been used[2]. As we see from (5.5), the quantities $E^t_+(-i\alpha_i)$ are real. Consider the function

$$\psi(t) = \phi(t) + \frac{1}{2}\mathbf{e}^\top\mathbf{C}\mathbf{e} = \phi(t) + \frac{1}{2}\mathbf{e}\cdot\mathbf{C}\mathbf{e}, \tag{5.25}$$

where $\phi(t)$ is the equilibrium free energy and $\mathbf{C}$ is a symmetric, positive definite matrix with components C_{ij}, $i,j = 1,2,\ldots,n$. It is clear that $\psi(t)$ has property P2 of a free energy, given by (2.7). For a stationary history $E^t(s) = E(t)$, $s\in\mathbb{R}^+$, we have, from (3.10), that $E^t_+(-i\alpha_i) = E(t)/\alpha_i$, so that $e_i(t) = 0$, $i = 1, 2,\ldots,n$. Relations (2.6) and (4.13) yield the condition

$$\sum_{j=1}^{n} C_{ij} = G_i, \quad i = 1,2,\ldots,n. \tag{5.26}$$

From $(3.13)_1$ or (5.24), we have

$$\dot{e}_i(t) = \dot{E}(t) - \alpha_i e_i(t), \quad i = 1,2,\ldots,n, \tag{5.27}$$

so that, using (5.26), we obtain

$$\begin{aligned} &\dot{\psi}(t) + D(t) = T(t)\dot{E}(t), \\ &D(t) = \tfrac{1}{2}\mathbf{e}^\top\Gamma\mathbf{e}, \qquad \Gamma_{ij} = (\alpha_i+\alpha_j)C_{ij}, \end{aligned} \tag{5.28}$$

where Γ_{ij} are the elements of the matrix Γ. Condition P3 (see (2.9)) requires that Γ must be at least positive semidefinite.

5.3 Properties of I^t in the frequency domain

Let us revert now to discussing general materials but returning periodically to the discrete spectrum case as an illustrative example. Some results presented here

[2] Note that analytic continuation into Ω^- is straightforward since E^t_+ is analytic in this half-plane.

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are the same as or equivalent to certain formulae given previously in [1, 6]. Let

$$I_k^t(\tau) = \frac{d^k}{d\tau^k} I^t(\tau), \quad k = 1, 2, \ldots, \tag{5.29}$$

so that

$$\begin{aligned} I_1^t(\tau) &= \int_0^\infty G'(\tau + u)\dot{E}^t(u)du, \\ I_2^t(\tau) &= \int_0^\infty G''(\tau + u)\dot{E}^t(u)du. \end{aligned} \tag{5.30}$$

Also,

$$\begin{aligned} \frac{\partial}{\partial t} I_1^t(s) &= G'(s)\dot{E}(t) + I_2^t(s), \\ \frac{\partial}{\partial t} I_2^t(s) &= G''(s)\dot{E}(t) + I_3^t(s). \end{aligned} \tag{5.31}$$

Just as in (5.2), we have

$$\lim_{\tau\to\infty} I_k^t(\tau) = 0, \quad k = 1, 2, 3, \ldots. \tag{5.32}$$

The quantity $I^t(s), s \in \mathbb{R}$, will be required. This can be defined in a number of ways. We choose the following formula. Let

$$I^t(s) = \int_0^\infty \widetilde{G}(|s + u|)\dot{E}^t(u)du, \quad s \in \mathbb{R}. \tag{5.33}$$

Then

$$\begin{aligned} I_2^t(s) &= \int_0^\infty \frac{\partial^2}{\partial s^2} G(|s + u|)\dot{E}^t(u)du, \\ \frac{\partial}{\partial t} I_2^t(s) &= \frac{\partial^2}{\partial s^2} G(|s|)\dot{E}(t) + I_3^t(s), \quad s \in \mathbb{R}. \end{aligned} \tag{5.34}$$

Note that

$$\lim_{|s|\to\infty} I_k^t(s) = 0, \quad k = 1, 2, 3, \ldots. \tag{5.35}$$

We now seek to express I^t in terms of frequency domain quantities. Let us put

$$\widetilde{G}(u) = 0, \quad \dot{E}^t(u) = 0, \quad u \in \mathbb{R}^{--}. \tag{5.36}$$

Then

$$\begin{aligned} \int_{-\infty}^{\infty} \widetilde{G}(u + \tau)e^{-i\omega u}du &= \int_0^\infty \widetilde{G}(v)e^{-i\omega v}dv\, e^{i\omega\tau} \\ &= \widetilde{G}_+(\omega)\, e^{i\omega\tau}. \end{aligned} \tag{5.37}$$

Parseval's formula, applied to $(5.1)_5$, gives

$$I^t(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \overline{\widetilde{G}_+(\omega)}\dot{E}_+^t(\omega)e^{-i\omega\tau}d\omega, \quad \tau \geq 0. \tag{5.38}$$

We have

$$I^t(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} [\overline{\widetilde{G}_+(\omega)} + \lambda\widetilde{G}_+(\omega)]\dot{E}_+^t(\omega)e^{-i\omega\tau}d\omega, \tag{5.39}$$

for arbitrary complex values of λ, since the added term gives zero. This can be seen by integrating over a contour around $\Omega^{(-)}$, noting that the exponential goes to zero as $Im\omega \to -\infty$ and using (3.15). Let us choose $\lambda = 1$. Then, recalling $(3.5)_1$, we find that

$$\begin{aligned} I^t(\tau) &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} \dot{E}_+^t(\omega)e^{-i\omega\tau}d\omega \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} \overline{\dot{E}_+^t(\omega)}e^{i\omega\tau}d\omega, \end{aligned} \tag{5.40}$$

for $\tau \geq 0$, where the reality of I^t has been used. This relation generalizes (3.17). It follows that

$$\begin{aligned} I_+^t(\omega) &= \int_0^\infty I^t(\tau)e^{-i\omega\tau}d\tau \\ &= -\frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{H(\omega')\overline{\dot{E}_+^t(\omega')}}{(\omega')^2(\omega' - \omega^-)} d\omega'. \end{aligned} \tag{5.41}$$

We must choose ω^- so that the integration over the exponential converges. From $(5.1)_3$, it follows that $I_+^t(\omega)$ is a FMS. Similarly, the derivatives of $I^t(s)$, given by (5.29), for $s \in \mathbb{R}^+$ are also FMSs, in particular $I_{1+}^t(\omega)$ and $I_{2+}^t(\omega)$.

For the discrete spectrum case, it follows from (5.6) that

$$I_+^t(\omega) = -i \sum_{i=1}^n \frac{G_i \dot{E}_+^t(-i\alpha_i)}{\omega - i\alpha_i}. \tag{5.42}$$

By virtue of remark 5.3, equation (5.42) implies that $I_+^t(\omega)$ is a FMS, which confirms for such materials the general property stated after (5.41).

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Similarly, let I^t be defined by (5.39) for $\tau < 0$. In this case, we cannot close the contour in $\Omega^{(-)}$ because the exponential diverges on this half-plane. It follows that $I^t(\tau)$ depends on λ for $\tau < 0$. Let us take $\lambda = 1$ so that it is given by (5.40) for $\tau < 0$. This is equivalent to the choice given by (5.33), as may be seen by transforming the integration variable in (5.33) from u to $-u$ and using (3.7) together with the convolution theorem. Also,

$$\begin{aligned} I^t_-(\omega) &= \int_{-\infty}^{0} I^t(\tau) e^{-i\omega\tau} d\tau \\ &= \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{H(\omega') \overline{\dot{E}^t_+}(\omega')}{(\omega')^2(\omega' - \omega^+)} d\omega', \end{aligned} \tag{5.43}$$

and

$$\begin{aligned} I^t_F(\omega) &= I^t_-(\omega) + I^t_+(\omega) \\ &= \int_{-\infty}^{\infty} I^t(\tau) e^{-i\omega\tau} d\tau = \frac{2H(\omega)}{\omega^2} \overline{\dot{E}^t_+}(\omega), \end{aligned} \tag{5.44}$$

by virtue of the Plemelj formulae (3.19) and (3.20). It follows from (5.44) that I^t_- is not a FMS. Also, one can deduce from $(3.13)_1$ and (5.44) that

$$\dot{I}^t_F(\omega) = i\omega I^t_F(\omega) + 2\frac{H(\omega)}{\omega^2} \dot{E}(t). \tag{5.45}$$

We see, using (3.6) and (3.15), that

$$I^t_F(\omega) \sim \omega^{-3}, \tag{5.46}$$

at large ω.

Note that (5.44) allows us to write (3.17) in the form

$$\begin{aligned} T(t) &= T_e(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \overline{I^t_F}(\omega) d\omega \\ &= T_e(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} I^t_F(\omega) d\omega. \end{aligned} \tag{5.47}$$

For the discrete spectrum case, we have from $(4.14)_1$, (5.42) and (5.44) that

$$\begin{aligned} I^t_-(\omega) &= I^t_F(\omega) - I^t_+(\omega) \\ &= i \sum_{i=1}^{n} \frac{G_i[\dot{E}^t_+(-i\alpha_i) - \overline{\dot{E}^t_+}(\omega)]}{\omega - i\alpha_i} + i \sum_{i=1}^{n} \frac{G_i \overline{\dot{E}^t_+}(\omega)}{\omega + i\alpha_i}, \end{aligned} \tag{5.48}$$

which is analytic on $\Omega^{(+)}$. Returning to general materials, we see from $(5.40)_2$ that

$$\begin{aligned} I^t_1(\tau) &= -\frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega} \overline{\dot{E}^t_+}(\omega) e^{i\omega\tau} d\omega, \\ I^t_2(\tau) &= -\frac{1}{\pi} \int_{-\infty}^{\infty} H(\omega) \overline{\dot{E}^t_+}(\omega) e^{i\omega\tau} d\omega, \quad \tau \geq 0. \end{aligned} \tag{5.49}$$

Thus

$$\begin{aligned} I^t_{1\pm}(\omega) &= \mp\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega') \overline{\dot{E}^t_+}(\omega')}{\omega'(\omega' - \omega^{\mp})} d\omega', \\ I^t_{2\pm}(\omega) &= \pm\frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{H(\omega') \overline{\dot{E}^t_+}(\omega')}{\omega' - \omega^{\mp}} d\omega', \\ I^t_{1F}(\omega) &= i\omega I^t_F(\omega), \quad I^t_{2F}(\omega) = -\omega^2 I^t_F(\omega). \end{aligned} \tag{5.50}$$

We have

$$I^t_{2F}(\omega) = -2H(\omega)\overline{\dot{E}^t_+}(\omega) = I^t_{2+}(\omega) + I^t_{2-}(\omega), \tag{5.51}$$

by virtue of (5.44) and the Plemelj formulae (3.19) and (3.20). The quantities I^t_+, I^t_{1+} and I^t_{2+} are analytic in Ω^- while I^t_-, I^t_{1-} and I^t_{2-} are analytic in Ω^+. For the complex conjugate of these quantities, the opposite is true.

In the case of discrete spectrum materials, we have, from (5.6),

$$\begin{aligned} I^t_1(\tau) &= -\sum_{i=1}^{n} \alpha_i G_i \dot{E}^t_+(-i\alpha_i) e^{-\alpha_i\tau} \\ I^t_2(\tau) &= \sum_{i=1}^{n} \alpha_i^2 G_i \dot{E}^t_+(-i\alpha_i) e^{-\alpha_i\tau}, \end{aligned} \tag{5.52}$$

and

$$\begin{aligned} I^t_{1+}(\omega) &= i \sum_{i=1}^{n} \frac{\alpha_i G_i}{\omega - i\alpha_i} \dot{E}^t(-i\alpha_i), \\ I^t_{2+}(\omega) &= -i \sum_{i=1}^{n} \frac{\alpha_i^2 G_i}{\omega - i\alpha_i} \dot{E}^t(-i\alpha_i). \end{aligned} \tag{5.53}$$

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The corresponding quantities $I^t_{1-}(\omega)$ and $I^t_{2-}(\omega)$ can be given in the same way as (5.48).

5.4 Frequency domain representation of the work function

The frequency domain version of (2.22) is [1, 10]

$$\begin{aligned} W(t) &= \phi(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2}\left|\dot{E}^t_+(\omega)\right|^2 d\omega \\ &= \phi(t) + \frac{1}{8\pi}\int_{-\infty}^{\infty} \frac{\omega^2}{H(\omega)}\left|I^t_F(\omega)\right|^2 d\omega \qquad (5.54) \\ &= \phi(t) + \frac{1}{8\pi}\int_{-\infty}^{\infty} \frac{\left|I^t_{2F}(\omega)\right|^2}{\omega^2 H(\omega)} d\omega, \end{aligned}$$

by virtue of (5.44) and $(5.50)_4$.

6 Single integral quadratic forms in terms of I^t derivatives

Consider the functional

$$\psi(t) = \phi(t) + \frac{1}{2}\int_0^{\infty} L(\tau)[I^t_1(\tau)]^2 d\tau, \qquad (6.1)$$

in terms of $I_1(\tau)$, defined by $(5.30)_1$. This quantity is assumed to be a free energy. We now explore the constraints on $L(\tau)$ imposed by this requirement.

The relation (2.9) must hold. Using (2.13), $(5.31)_1$ and (5.32), we deduce that

$$\begin{aligned} \dot{\psi}(t) = \dot{E}(t)\left[T_e(t) + \int_0^{\infty} G'(\tau)L(\tau)I^t_1(\tau)d\tau\right] \\ + \int_0^{\infty} I^t_2(\tau)L(\tau)I^t_1(\tau)d\tau = T(t)\dot{E}(t) \\ -\frac{1}{2}L(0)[I^t_1(0)]^2 - \frac{1}{2}\int_0^{\infty} L'(\tau)[I^t_1(\tau)]^2 d\tau, \qquad (6.2) \end{aligned}$$

provided that the condition

$$\int_0^{\infty} G'(\tau)L(\tau)I^t_1(\tau)d\tau = T(t) - T_e(t) \qquad (6.3)$$

holds. With the help of (2.3), (5.3) and $(5.30)_1$, this can be written as

$$\begin{aligned} &\int_0^{\infty} [G'(\tau)L(\tau) + 1]I^t_1(\tau)d\tau \\ &= \int_0^{\infty}\int_0^{\infty} [G'(\tau)L(\tau) + 1]G'(\tau + u)\dot{E}^t(u)d\tau du = 0, \end{aligned} \qquad (6.4)$$

which must be true for arbitrary histories. Let us write the resulting condition as an integral equation of the form

$$\int_0^{\infty} G'(\tau + u)f(\tau)d\tau = 0 \quad \forall u \in \mathbb{R}^+,$$

$$f(\tau) = G'(\tau)L(\tau) + 1. \qquad (6.5)$$

An alternative pathway to (6.5) is to express (6.1) in the form (2.14) with

$$\widetilde{G}(s,u) = \int_0^{\infty} G'(\tau + s)L(\tau)G'(\tau + u)d\tau, \qquad (6.6)$$

and to impose the constraint (2.16), written in terms of $\widetilde{G}(u)$. Condition (6.5) has the same form as (5.7), leading to

$$\frac{2i}{\omega}H(\omega)f_+(\omega) = J_+(\omega), \qquad (6.7)$$

where $J_+(\omega)$ is an unknown function, analytic in $\Omega^{(-)}$. This corresponds to (5.10).

If the material has only isolated singularities, taken here to be the discrete spectrum type, in accordance with remark 5.2, we see that there are many non-trivial solutions of (6.5) given by a form similar to (5.18). However, in this case, there is no reason for $f(0)$ to be zero, so that, at large ω,

$$f_+(\omega) \sim \frac{f(0)}{i\omega}. \qquad (6.8)$$

which differs from (5.17). Thus, we put

$$f_+(\omega) = -\frac{if_0}{\omega - i\chi_0}\prod_{j=1}^{n}\left\{\frac{\omega + i\alpha_j}{\omega - i\chi_j}\right\}, \quad f_0 = f(0), \qquad (6.9)$$

where the constants χ_i, $i = 0, 1, \ldots, n$ are arbitrary positive quantities. Also, f_0 may be chosen arbitrarily.

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Remark 6.1 The observations before (5.17) and at the end of subsection 5.1 on more general choices of $E_{d+}(\omega)$ do not apply to $f_+(\omega)$. This is because for $f(\tau)$, given by $(6.5)_2$, a material with only isolated singularities cannot have branch cuts in the Fourier transform of the quantities $G'(\tau)$ and $L(\tau)$. Thus, (6.9) is the most general form of $f_+(\omega)$ for discrete spectrum materials.

Note that if we choose $\chi_i = \gamma_i$, $i = 1, 2, \ldots, n$ then

$$f_+(\omega) = -\frac{if_0 h_\infty}{(\omega - i\chi_0)H_-^N(\omega)}, \tag{6.10}$$

where $H_-^N(\omega)$ is given by (4.21) and χ_0 is an arbitrary non-negative quantity.

The quantity $f(\tau)$ is the inverse transform of $f_+(\omega)$. It follows from $(6.5)_2$ that

$$L(\tau) = -\frac{1}{G'(\tau)} + \frac{f(\tau)}{G'(\tau)}, \quad \tau \in \mathbb{R}^+. \tag{6.11}$$

We deduce from (2.9) and (6.2) that the rate of dissipation is given by

$$D(t) = \frac{1}{2}L(0)[I_1^t(0)]^2 + \frac{1}{2}\int_0^\infty L'(\tau)[I_1^t(\tau)]^2 d\tau. \tag{6.12}$$

In order that $\psi(t) - \phi(t)$ and $D(t)$ be non-negative, we must have

$$L(s) \geq 0, \qquad L'(s) \geq 0, \qquad \forall s \in \mathbb{R}^+. \tag{6.13}$$

Note that, from (4.11), the relaxation function of the material obeys the constraints

$$G'(s) \leq 0, \qquad G''(s) \geq 0, \quad \forall s \in \mathbb{R}^+. \tag{6.14}$$

The quantity $L(\tau)$, given by (6.11), obeys (6.13) if

$$f(s) \leq 1, \quad \frac{f'(s)}{f(s) - 1} \geq \frac{G''(s)}{G'(s)}, \quad \forall s \in \mathbb{R}^+. \tag{6.15}$$

If the free energies of the form (6.1) are to exist, based on $(6.5)_2$ with $f(s)$ non-zero, we must show that the set of functions $f(\cdot)$, obeying the conditions (6.15), is not empty. We can write (6.9) in the form

$$\begin{aligned}
&f_+(\omega) = -if_0 \sum_{i=0}^{n} \frac{B_i}{\omega - i\chi_i}, \\
&B_i = \frac{\chi_i + \alpha_i}{\chi_i - \chi_0} \prod_{\substack{j=1 \\ j \neq i}}^{n} \left\{ \frac{\chi_i + \alpha_j}{\chi_i - \chi_j} \right\}, \quad i = 1, 2, \ldots, n, \\
&B_0 = \prod_{j=1}^{n} \left\{ \frac{\chi_0 + \alpha_j}{\chi_0 - \chi_j} \right\}, \quad \sum_{i=0}^{n} B_i = 1,
\end{aligned} \tag{6.16}$$

where the last relation follows from (6.8). Taking the inverse Fourier transform of $(6.16)_1$, we obtain that

$$f(s) = f_0 \sum_{i=0}^{n} B_i e^{-\chi_i s}, \quad s \in \mathbb{R}^+. \tag{6.17}$$

It may be confirmed from (6.16) that a relation similar to (5.23) holds. The coefficients B_i alternate in sign, so that $f(s)$ and $f'(s)$ may take both positive and negative values. However, by taking $|f_0|$ to be sufficiently small, we can ensure that $(6.15)_1$ holds, as may be seen by the following argument. Let

$$\begin{aligned}
&f(s) = f_0[T_1(s) - T_2(s)], \\
&T_1(s) = \textstyle\sum_{B_i > 0} B_i e^{-\chi_i s}, \quad T_2(s) = -\textstyle\sum_{B_i < 0} B_i e^{-\chi_i s}.
\end{aligned} \tag{6.18}$$

Both $T_1(s)$ and $T_2(s)$ are positive quantities, decaying monotonically to zero at large s. Let $f_0 > 0$ ($f_0 < 0$). Then, if we choose

$$f_0 \leq \frac{1}{T_1(0)} \quad \left(|f_0| \leq \frac{1}{T_2(0)}\right), \tag{6.19}$$

condition $(6.15)_1$ holds. We choose f_0 so that $f(s) < 1$, $s \in \mathbb{R}^+$ by choosing the inequalities in (6.19) to be strict. It follows that

$$M_1 = \min_{s \in \mathbb{R}^+} |f_0[T_1(s) - T_2(s)] - 1| > 0. \tag{6.20}$$

Now, from (4.11), we have

$$-\frac{G''(s)}{G'(s)} \in [a, b] \quad \forall s \in \mathbb{R}^+, \tag{6.21}$$

where a, b are positive quantities, obeying $a < b$. Let $f_0 > 0$. We put

$$\begin{aligned}
&f'(s) = f_0[-T_3(s) + T_4(s)], \\
&T_3(s) = \textstyle\sum_{B_i > 0} B_i \chi_i e^{-\chi_i s} \geq 0, \quad T_4(s) = -\textstyle\sum_{B_i < 0} B_i \chi_i e^{-\chi_i s} \geq 0.
\end{aligned} \tag{6.22}$$

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Then $(6.15)_2$ is satisfied if

$$\frac{f_0[T_3(s)-T_4(s)]}{|f_0[T_1(s)-T_2(s)]-1|} > -a, \tag{6.23}$$

or

$$f_0[T_3(s)-T_4(s)] > -a|f_0[T_1(s)-T_2(s)]-1|. \tag{6.24}$$

This will be true if

$$f_0[T_3(s)-T_4(s)] > -aM_1. \tag{6.25}$$

where M_1 is defined by (6.20). Let

$$M_2 = \min_{s\in\mathbb{R}^+}[T_3(s)-T_4(s)]. \tag{6.26}$$

If $M_2 \geq 0$, then (6.24) holds. If $M_2 < 0$, we choose

$$f_0 < a\frac{M_1}{|M_2|}, \tag{6.27}$$

to ensure that $(6.15)_2$ holds. If $f_0 < 0$, we define

$$M_2 = \min_{s\in\mathbb{R}^+}[T_4(s)-T_3(s)]. \tag{6.28}$$

and (6.27) is replaced by

$$|f_0| < a\frac{M_1}{|M_2|}. \tag{6.29}$$

For materials where $n = 1$, all free energies which are FMSs reduce to the same form [2]. It can be shown easily that for $L(\tau)$ given by (6.31) below, the functional defined in (6.1) has this form, so that the extra quadratic form involving $f(\tau)$ cannot contribute. We see that (6.17) is given by

$$\begin{aligned} &f(s) = f_0[B_0e^{-\chi_0 s} + B_1e^{-\chi_1 s}],\\ &B_0 = -\frac{\chi_0+\alpha}{\chi_1-\chi_0}, \quad B_1 = \frac{\chi_1+\alpha}{\chi_1-\chi_0},\\ &B_0 = 1 - B_1, \quad B_1 > 1, \end{aligned} \tag{6.30}$$

for $n = 1$. Using $(5.52)_1$, it is straightforward to show that the resulting contribution to (6.1) indeed vanishes.

If the material has branch cut singularities, then $f(\tau) = 0$, $\tau \in \mathbb{R}^+$ is the only solution of (6.5), so that

$$L(\tau) = -\frac{1}{G'(\tau)}, \quad \tau \in \mathbb{R}^+, \tag{6.31}$$

and the only possibility for a free energy given by a single integral quadratic form is the quantity ψ_F, introduced in [6]. This functional and the associated rate of dissipation have the forms

$$\psi_F(t) = \phi(t) - \frac{1}{2}\int_0^\infty \frac{[I_1^t(\tau)]^2}{G'(\tau)}d\tau, \tag{6.32}$$

and

$$\begin{aligned} D_F(t) &= -\frac{1}{2}\frac{[I_1^t(0)]^2}{G'(0)} - \frac{1}{2}\int_0^\infty \left[\frac{d}{d\tau}\frac{1}{G'(\tau)}\right][I_1^t(\tau)]^2 d\tau\\ &= -\frac{1}{2}\frac{[I_1^t(0)]^2}{G'(0)} + \frac{1}{2}\int_0^\infty G''(\tau)\left[\frac{I_1^t(\tau)}{G'(\tau)}\right]^2 d\tau. \end{aligned} \tag{6.33}$$

These quantities are non-negative and $\psi_F(t)$ is a valid free energy if conditions (6.14) hold, not only for materials with branch point singularities, but for all materials. It is a relatively simple functional, convenient for applications.

For materials with only isolated singularities, a more general choice of $L(s)$, given by (6.11), also produces valid free energy functionals, provided that the inequalities (6.15) are enforced. This can be done by ensuring that f_0 obeys (6.19) and (6.27) or (6.29), for any given choices of the quantities χ_i, $i = 0, 1, \ldots, n$. The necessity to enforce such conditions renders these choices less convenient for practical applications.

7 Double integral quadratic forms in terms of I^t derivatives: time domain representations

We now discuss double integral quadratic forms for free energies and rates of dissipation. The time domain formulation is explored in this section, while the corresponding frequency domain relations are presented in the next.

Consider the form

$$\psi(t) = \phi(t) + \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)L(s,u)I_2^t(u)\,ds\,du, \tag{7.1}$$

There is no loss of generality in putting

$$L(s,u) = L(u,s). \tag{7.2}$$

The assumptions

$$\begin{aligned} &L(\cdot,\cdot) \in L^1(\mathbb{R}^+\times\mathbb{R}^+) \cap \mathrm{L}^2(\mathbb{R}^+\times\mathbb{R}^+),\\ &\lim_{s\to\infty} L(s,u) = \lim_{s\to\infty} L(u,s) = 0 \end{aligned} \tag{7.3}$$

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will be adopted. It is understood that $L(s,u)$ vanishes for negative values of s and u. We have from (2.13) and $(5.31)_2$ that

$$\dot{\psi}(t) = \dot{E}(t)\left[T_e(t) + \frac{1}{2}\int_0^\infty\int_0^\infty G''(s)L(s,u)I_2^t(u)dsdu + \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)L(s,u)G''(u)dsdu\right] + \frac{1}{2}\int_0^\infty\int_0^\infty I_3^t(s)L(s,u)I_2^t(u)dsdu + \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)L(s,u)I_3^t(u)dsdu. \tag{7.4}$$

It is assumed that

$$L(0,u) = L(s,0) = 0. \tag{7.5}$$

This property greatly simplifies the next step of the argument, making possible an analogy with the history based formalism presented in [10].

The two integrals in brackets in (7.4) can be shown to be equal by interchanging integration variables. Applying partial integrations and using (5.32), we obtain

$$\dot{\psi}(t) = \dot{E}(t)\left[T_e(t) + \int_0^\infty\int_0^\infty G''(s)L(s,u)I_2^t(u)dsdu\right] - \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)[L_1(s,u) + L_2(s,u)]I_2^t(u)dsdu. \tag{7.6}$$

It is assumed in general that

$$\int_0^\infty\int_0^\infty G''(s)L(s,u)I_2^t(u)dsdu = \int_0^\infty \widetilde{G}(s)\dot{E}^t(s)ds, \tag{7.7}$$

for arbitrary choices of histories. Using $(5.30)_2$, this leads to the condition

$$\int_0^\infty\int_0^\infty G''(s)L(s,u)G''(u+v)dsdu = \widetilde{G}(v). \tag{7.8}$$

This can also be derived in an alternative manner. We observe from (2.14), $(5.30)_2$ and (7.1) that

$$\widetilde{G}(s,u) = \int_0^\infty\int_0^\infty G''(s+s_1)L(s_1,u_1)G''(u_1+u)ds_1du_1. \tag{7.9}$$

This relation corresponds to (6.6). Applying (2.16) gives (7.8). Let

$$m(u) = \int_0^\infty G''(s)L(s,u)ds, \tag{7.10}$$

noting that $m(0) = 0$, by virtue of (7.5). Then, with the aid of a partial integration, (7.8) can be expressed as

$$\int_0^\infty G'(s+u)f(u)du = 0, \quad \forall s \in \mathbb{R}^+,$$

$$f(u) = 1 - m'(u) = 1 - \int_0^\infty G''(s)L_2(s,u)ds = 1 + \int_0^\infty G'(s)L_{12}(s,u)ds, \tag{7.11}$$

which corresponds to (6.5). Note that Remark 6.1 also applies here. Referring to $(2.3)_1$ and (2.9), equation (7.6) can be written as

$$\dot{\psi}(t) + D(t) = T(t)\dot{E}(t),$$

$$D(t) = \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)R(s,u)I_2^t(u)dsdu, \tag{7.12}$$

$$R(s,u) = L_1(s,u) + L_2(s,u) = R(u,s).$$

The kernels $L(s,u)$ and $R(s,u)$ must be such as to render the integral terms in (7.1) and $(7.12)_2$ non-negative.

The work function cannot be expressed in terms of $I_2^t(s)$, $s \geq 0$, but can be given in terms of this quantity for $s \in \mathbb{R}$. This follows from the frequency representation (5.54). We write

$$W(t) = \phi(t) + \frac{1}{2}\int_{-\infty}^\infty I_2^t(s)J(|s-u|)I_2^t(u)dsdu, \tag{7.13}$$

where the kernel $J(|u|)$ is related to the inverse transform of the kernel in $(5.54)_3$. Convergence issues in this context must be handled carefully.

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It follows from (2.10) that the total dissipation must also depend on $I_2^t(s)$, $s \in \mathbb{R}$. We write

$$\mathfrak{D}(t) = \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} I_2^t(s)V(s,u)I_2^t(u)dsdu,$$
$$V(s,u) = V(u,s), \tag{7.14}$$

where, to satisfy (2.10), we must have

$$V(s,u) = \begin{cases} J(|s-u|), & s<0 \quad \text{or} \quad u<0, \\ -L(s,u) + J(|s-u|), & s>0 \quad \text{and} \quad u>0. \end{cases} \tag{7.15}$$

Note that $V(s,u)$ is continuous at $s=0$ and $u=0$. Also,

$$V_1(s,u) + V_2(s,u) = -L_1(s,u) - L_2(s,u) = -R(s,u). \tag{7.16}$$

Differentiating (7.14) with respect to time and using $(5.34)_2$, we obtain

$$\dot{\mathfrak{D}}(t) = D(t), \tag{7.17}$$

where $D(t)$ is given by (7.12), provided that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\partial^2}{\partial s^2}G(|s|)V(s,u)I_2^t(u)dsdu = 0. \tag{7.18}$$

This condition must hold for arbitrary histories, which yields

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\partial^2}{\partial s^2}G(|s|)V(s,u)\frac{\partial^2}{\partial u^2}G(|u+v|)dsdu = 0.$$
$$v \in \mathbb{R}^+. \tag{7.19}$$

We see that $Q(s,u)$ in (2.21) is given by

$$Q(s,u) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\partial^2}{\partial s^2}G(|s+s_1|)V(s_1,u_1)$$
$$\frac{\partial^2}{\partial u^2}G(|u_1+u|)ds_1du_1, \tag{7.20}$$

so that (7.19) is equivalent to (2.26).

Relationships (7.13)–(7.20) are incomplete without specifying the forms of the kernels more precisely. This is difficult in the time domain. The natural framework for a deeper treatment of such issues is the frequency domain, as is clear from (5.54), and will be further demonstrated in Sect. 8.

7.1 Free energy kernel in terms of the dissipation kernel

Results were obtained in [10] which allowed the kernel of the quadratic form (2.14) to be determined in terms of the kernel of (2.18). A corresponding theory was also given in terms of frequency domain quantities, which proved more useful for applications. We now adapt this method to apply to functionals that are quadratic in I^t. It will emerge that the new technique does not lead to new free energies. However, it is useful in the context of dealing with the minimum free energy.

Let us treat $(7.12)_3$ as a first order partial differential equation for $L(s,u)$, $s,u \in \mathbb{R}^+$, where $R(s,u)$, $s,u \in \mathbb{R}^+$ is presumed to be known. We introduce new variables,

$$x = s+u \geq 0, \quad y = s-u, \tag{7.21}$$

in terms of which $(7.12)_3$ becomes

$$\frac{\partial}{\partial x}L_n(x,y) = \frac{1}{2}R_n(x,y), \quad L_n(x,y) = L(s,u),$$
$$R_n(x,y) = R(s,u), \tag{7.22}$$

with general solution

$$L_n(x,y) = L_n(x_0,y) + \frac{1}{2}\int_{x_0}^{x} R_n(x',y)dx' \tag{7.23}$$

where x_0 is an arbitrary non-negative real quantity. It follows from (7.2) and $(7.12)_4$ that

$$L_n(x,y) = L_n(x,-y) = L_n(x,|y|),$$
$$R_n(x,y) = R_n(x,-y) = R_n(x,|y|). \tag{7.24}$$

Observe that, by virtue of (7.5),

$$L_n(u,u) = L_n(u,-u) = L_n(u,|u|) = 0, \quad u \in \mathbb{R}^+. \tag{7.25}$$

Putting

$$x' = s'+u' \geq 0, \quad y = s'-u' = s-u, \tag{7.26}$$

we have

$$s' = \frac{1}{2}(x'+y), \quad u' = \frac{1}{2}(x'-y),$$
$$R_n(x',y) = R\left(\frac{1}{2}(x'+y), \frac{1}{2}(x'-y)\right), \tag{7.27}$$

so that (7.23) and (7.25) give

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$$L(s,u) = L_n(x,y) = \frac{1}{2}\int_{|y|}^{x} R_n(x',y)dx'$$
$$= \int_0^{\min(s,u)} R(s-v,u-v)dv, \qquad (7.28)$$

which, as expected, obeys (7.5). Relation (7.1) gives

$$\psi(t) = \phi(t) + \frac{1}{2}\int_0^\infty\int_0^\infty I_2^t(s)$$
$$\int_0^{\min(s,u)} R(s-v,u-v)dvI_2^t(u)dsdu$$
$$= \phi(t) + \frac{1}{2}\int_0^\infty\int_0^\infty\int_0^\infty I_2^t(s)R(s-v,u-v)I_2^t(u)dvdsdu, \qquad (7.29)$$

since $R(s-v,u-v)=0$ for $v>\min(s,u)$. Let us assume that we have chosen $R(\cdot,\cdot)$ so that $D(t)$, given by $(7.12)_2$, is non-negative for any choice of I_2^t. For $v \geq 0$ and arbitrary choices of I_2^t, we have

$$\int_0^\infty\int_0^\infty I_2^t(s)R(s-v,u-v)I_2^t(u)dsdu$$
$$= \int_0^\infty\int_0^\infty I_2^t(s_1+v)R(s_1,u_1)I_2^t(u_1+v)ds_1du_1$$
$$= \int_0^\infty\int_0^\infty f(s_1)R(s_1,u_1)f(u_1)ds_1du_1 \geq 0, \qquad (7.30)$$

where $f(s_1) = I_2^t(s_1+v)$ and is therefore arbitrary. It follows that the integral in $(7.29)_2$ is also non-negative. Therefore, $L(\cdot,\cdot)$, given by (7.28), has the property that the integral term in (7.1) is non-negative. Thus, the basic strategy developed in [10] is valid here also. The idea is to assign $R(\cdot,\cdot)$ so that the rate of dissipation is non-negative. Then, the associated free energy, *i.e.* that with kernel given by (7.28), also has the required positivity property. It will emerge however that the strategy developed in [10] is not useful in the present case, except in the context of the minimum free energy.

We note the similarity between the expression (7.28) and the kernel of the expression for the total dissipation in [10].

8 Double integral quadratic forms in terms of I^t derivatives: frequency domain representations

The initial results presented here are analogous to those in [10]. We define

$$L_{+-}(\omega_1,\omega_2) = \int_0^\infty\int_0^\infty L(s,u)e^{-i\omega_1 s+i\omega_2 u}dsdu$$
$$= \overline{L_{+-}}(\omega_2,\omega_1),$$
$$R_{+-}(\omega_1,\omega_2) = \int_0^\infty\int_0^\infty R(s,u)e^{-i\omega_1 s+i\omega_2 u}dsdu$$
$$= \overline{R_{+-}}(\omega_2,\omega_1),$$
$$V_F(\omega_1,\omega_2) = \int_{-\infty}^\infty\int_{-\infty}^\infty V(s,u)e^{-i\omega_1 s+i\omega_2 u}dsdu$$
$$= \overline{V_F}(\omega_2,\omega_1), \qquad (8.1)$$

where L is introduced in (7.1), R is defined by $(7.12)_3$ and V by (7.15). The functions $L_{+-}(\omega_1,\omega_2)$ and $R_{+-}(\omega_1,\omega_2)$ are analytic in the lower half of the ω_1 complex plane and in the upper half of the ω_2 plane. The quantity $V_F(\omega_1,\omega_2)$ may have singularities anywhere in the ω_1 and ω_2 complex planes. Inverting Fourier transforms in (8.1) yields that

$$L(s,u) = \frac{1}{4\pi^2}\int_{-\infty}^\infty\int_{-\infty}^\infty L_{+-}(\omega_1,\omega_2)e^{i\omega_1 s-i\omega_2 u}d\omega_1 d\omega_2,$$
$$R(s,u) = \frac{1}{4\pi^2}\int_{-\infty}^\infty\int_{-\infty}^\infty R_{+-}(\omega_1,\omega_2)e^{i\omega_1 s-i\omega_2 u}d\omega_1 d\omega_2,$$
$$V(s,u) = \frac{1}{4\pi^2}\int_{-\infty}^\infty\int_{-\infty}^\infty V_F(\omega_1,\omega_2)e^{i\omega_1 s-i\omega_2 u}d\omega_1 d\omega_2. \qquad (8.2)$$

Note that, for complex values of the frequencies,

$$\overline{L_{+-}(\omega_1,\omega_2)} = L_{+-}(-\overline{\omega_1},-\overline{\omega_2}) = L_{+-}(\overline{\omega_2},\overline{\omega_1}), \qquad (8.3)$$

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with analogous relations for $R_{+-}(\omega_1,\omega_2)$ and $V_F(\omega_1,\omega_2)$. We define

$$
\begin{aligned}
&L_0(s) = L_1(0,s) = L_2(s,0),\\
&R(s,0) = R(0,s) = R(s) = L_0(s),\\
&L_{0+}(\omega) = \int_0^\infty L_0(s)e^{-i\omega s}ds, \qquad (8.4)\\
&R_+(\omega) = \int_0^\infty R(s)e^{-i\omega s}ds = L_{0+}(\omega).
\end{aligned}
$$

Relations (7.5) and $(7.12)_3$ have been used in deriving these connections. We have

$$\lim_{\omega\to\infty} i\omega L_{0+}(\omega) = L_0(0) = R(0,0). \tag{8.5}$$

Equations (7.5), $(7.12)_3$ and (8.1) give

$$i(\omega_1-\omega_2)L_{+-}(\omega_1,\omega_2) = R_{+-}(\omega_1,\omega_2), \tag{8.6}$$

which yields

$$L_{+-}(\omega_1,\omega_2) = \frac{R_{+-}(\omega_1,\omega_2)}{i(\omega_1^- - \omega_2^+)}, \tag{8.7}$$

on using the notation of (4.8). This choice, rather than that in (4.7), is dictated by the analytic properties of $L_{+-}(\omega_1,\omega_2)$. We refer to the analogous formula for the kernel of the total dissipation in [10].

Also

$$i(\omega_1-\omega_2)V_F(\omega_1,\omega_2) = -R_{+-}(\omega_1,\omega_2), \tag{8.8}$$

by virtue of (7.16). This gives an equation for $V_F(\omega_1,\omega_2)$ similar to (8.7) for $L_{+-}(\omega_1,\omega_2)$. The question which arises is whether the quantity in the denominator is $\omega_1^- - \omega_2^+$, as in (8.7), or $\omega_1^+ - \omega_2^-$. These are the only two possibilities. What they mean respectively is specified after (4.7). Now, the first choice would yield a quadratic form for the total dissipation equal to the negative of the integral term in the expression for the free energy (see (8.19) below). This would yield a meaningless result, so we take

$$V_F(\omega_1,\omega_2) = -\frac{R_{+-}(\omega_1,\omega_2)}{i(\omega_1^+ - \omega_2^-)}. \tag{8.9}$$

Another derivation of this result is given below; see (8.21).

Relation $(8.1)_2$ and the asymptotic behaviour of Fourier transforms [1, 10] yield that

$$R_{+-}(\omega_1,\omega_2) \sim \begin{cases} \dfrac{L_{0+}(\omega_1)}{-i\omega_2} & \text{as} \quad \omega_2\to\infty,\\[2mm] \dfrac{\overline{L_{0+}(\omega_2)}}{i\omega_1} & \text{as} \quad \omega_1\to\infty,\end{cases} \tag{8.10}$$

where $L_{0+}(\omega)$ is defined in (8.4). It follows from (8.7) that

$$L_{+-}(\omega_1,\omega_2) \sim \begin{cases} -\dfrac{L_{0+}(\omega_1)}{\omega_2^2} & \text{as} \quad \omega_2\to\infty,\\[2mm] -\dfrac{\overline{L_{0+}(\omega_2)}}{\omega_1^2} & \text{as} \quad \omega_1\to\infty.\end{cases} \tag{8.11}$$

The asymptotic behaviour of $V_F(\omega_1,\omega)$ is similar to (8.11), by virtue of (8.9). The condition corresponding to (7.5) is

$$
\begin{aligned}
&\int_{-\infty}^{\infty} L_{+-}(\omega_1,\omega)d\omega_1\\
&= \int_{-\infty}^{\infty} L_{+-}(\omega,\omega_2)d\omega_2 = 0 \quad \forall\omega\in\mathbb{R},
\end{aligned} \tag{8.12}
$$

which follows from Cauchy's theorem and (8.11).

It is shown in [10] that the free energy, the rate of dissipation and total dissipation, in terms of histories, are given by

$$
\begin{aligned}
\psi(t) &= \phi(t) + \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{\dot{E}^t_+}(\omega_1)\widetilde{G}_{+-}(\omega_1,\omega_2)\\
&\quad \dot{E}^t_+(\omega_2)d\omega_1 d\omega_2,\\
D(t) &= -\frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{\dot{E}^t_+}(\omega_1)K_{+-}(\omega_1,\omega_2)\dot{E}^t_+(\omega_2)d\omega_1 d\omega_2,\\
\mathfrak{D}(t) &= \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{\dot{E}^t_+}(\omega_1)Q_{+-}(\omega_1,\omega_2)\dot{E}^t_+(\omega_2)d\omega_1 d\omega_2,\\
&= \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{\dot{E}^t_+}(\omega_1)K_{+-}(\omega_1,\omega_2)\dot{E}^t_+(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2,
\end{aligned} \tag{8.13}
$$

where $\widetilde{G}_{+-}(\omega_1,\omega_2)$. $K_{+-}(\omega_1,\omega_2)$ and $Q_{+-}(\omega_1,\omega_2)$ are the Fourier transforms of $\widetilde{G}(s,u)$ in (2.14), $K(s,u)$ in (2.18), (2.19) and $Q(s,u)$ in (2.21). These are Fourier transforms as defined in (8.1).

We can write the frequency domain version of $(7.12)_2$ in the form

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$$
\begin{aligned}
D(t) &= \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{2+}}(\omega_1)R_{+-}(\omega_1,\omega_2) I^t_{2+}(\omega_2)d\omega_1 d\omega_2 \\
&= \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{2F}}(\omega_1)R_{+-}(\omega_1,\omega_2) I^t_{2F}(\omega_2)d\omega_1 d\omega_2 \\
&= \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{F}}(\omega_1)\omega_1^2\omega_2^2 R_{+-}(\omega_1,\omega_2) I^t_{F}(\omega_2)d\omega_1 d\omega_2.
\end{aligned}
\tag{8.14}
$$

where I^t_{2+}, I^t_F and I^t_{2F} are defined in $(5.50)_{2,4}$ and (5.44) respectively. The second form of (8.14) relies on (5.51) and the fact that

$$
\begin{aligned}
&\int_{-\infty}^{\infty} R_{+-}(\omega_1,\omega_2) I^t_{2-}(\omega_2)d\omega_2 \\
&= \int_{-\infty}^{\infty} \overline{I^t_{2-}}(\omega_1)R_{+-}(\omega_1,\omega_2)d\omega_1 = 0,
\end{aligned}
\tag{8.15}
$$

which are consequences of (8.10) and Cauchy's theorem. Using $(5.44)_3$, we can write $(8.14)_3$ as

$$
\begin{aligned}
D(t) &= \frac{1}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \dot{E}^t_{+}(\omega_1)H(\omega_1)H(\omega_2) R_{+-}(\omega_1,\omega_2)\overline{\dot{E}^t_{+}}(\omega_2)d\omega_1 d\omega_2 \\
&= \frac{1}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{\dot{E}^t_{+}}(\omega_1)H(\omega_1)H(\omega_2) R_{+-}(\omega_2,\omega_1)\dot{E}^t_{+}(\omega_2)d\omega_1 d\omega_2,
\end{aligned}
\tag{8.16}
$$

on interchanging integration variables. Comparing with $(8.13)_2$, we deduce that

$$
\begin{aligned}
-4H(\omega_1)H(\omega_2)R_{+-}(\omega_2,\omega_1) &= K_{+-}(\omega_1,\omega_2) \\
&+ k_{2+}(\omega_1,\omega_2) + k_{1-}(\omega_1,\omega_2),
\end{aligned}
\tag{8.17}
$$

where $k_{2+}(\omega_1,\omega_2)$ has singularities on the ω_2 complex plane only in $\Omega^{(+)}$ and $k_{1-}(\omega_1,\omega_2)$ has singularities on the ω_1 plane only in $\Omega^{(-)}$. They must also decay to zero at large ω_1, ω_2 but are otherwise arbitrary. This is an expression of the non-uniqueness of the kernels in the frequency domain, which is explored in [10], and which indeed apply to $R_{+-}(\omega_1,\omega_2)$ and $L_{+-}(\omega_1,\omega_2)$ in the present context. Using such non-uniqueness leads however to kernels that do not have the analytic properties possessed by R_{+-} and L_{+-}.

By analogy with (8.14) and (8.15), the frequency domain version of (7.1) takes the forms

$$
\begin{aligned}
\psi(t) &= \phi(t) + \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{2+}}(\omega_1)L_{+-}(\omega_1,\omega_2) I^t_{2+}(\omega_2)d\omega_1 d\omega_2 \\
&= \phi(t) + \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{2F}}(\omega_1)L_{+-}(\omega_1,\omega_2) I^t_{2F}(\omega_2)d\omega_1 d\omega_2 \\
&= \phi(t) + \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I^t_{F}}(\omega_1)\omega_1^2\omega_2^2 L_{+-}(\omega_1,\omega_2) I^t_{F}(\omega_2)d\omega_1 d\omega_2.
\end{aligned}
\tag{8.18}
$$

Note the all free energies and dissipations of the form (8.13) are expressible as quadratic forms in $I^t_F(\omega)$, by virtue of (5.44). However, in general, the analytic properties of the resulting kernels will not be given as in (8.14) and (8.18), so that the special forms $(8.14)_1$ and $(8.18)_1$ do not hold. It follows from (8.7) and (8.18) that

$$
\begin{aligned}
\psi(t) &= \phi(t) - \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{I^t_{2+}}(\omega_1)R_{+-}(\omega_1,\omega_2)I^t_{2+}(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2 \\
&= \phi(t) - \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{I^t_{2F}}(\omega_1)R_{+-}(\omega_1,\omega_2)I^t_{2F}(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2.
\end{aligned}
\tag{8.19}
$$

By virtue of the result proved in subsection 7.1, if R_{+-} is such that $D(t)$, given by (8.14), is non-negative, then

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$\psi(t) - \phi(t)$, given by (8.19), is also non-negative. Let us use (3.19) with respect to the integral in $(8.19)_2$ over ω_1 to obtain

$$\psi(t) = \phi(t) - \frac{i}{8\pi^2} P \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t(\omega_1)} R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2 + \frac{1}{8\pi} \int_{-\infty}^{\infty} \overline{I_{2F}^t(\omega)} R_{+-}(\omega,\omega) I_{2F}^t(\omega) d\omega. \tag{8.20}$$

The frequency domain version of (7.14), combined with (8.9), yields

$$\begin{aligned}\mathfrak{D}(t) &= \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t(\omega_1)} R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 \\ &= \frac{i}{8\pi^2} P \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t(\omega_1)} R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2 \\ &\quad + \frac{1}{8\pi} \int_{-\infty}^{\infty} \overline{I_{2F}^t(\omega)} R_{+-}(\omega,\omega) I_{2F}^t(\omega) d\omega.\end{aligned} \tag{8.21}$$

Alternatively, we can obtain this result by substituting for $K_{+-}(\omega_1,\omega_2)$ in $(8.13)_4$ from (8.17), noting that $k_{2+}(\omega_1,\omega_2)$ and $k_{1-}(\omega_1,\omega_2)$ do not contribute. This expression cannot be reduced to a quadratic form in $I_{2+}^t(\omega)$.

Relations (8.20), (8.21) and $(5.54)_3$ give (2.10) or

$$\psi(t) + \mathfrak{D}(t) = \phi(t) + \frac{1}{4\pi} \int_{-\infty}^{\infty} \overline{I_{2F}^t(\omega)} R_{+-}(\omega,\omega) I_{2F}^t(\omega) d\omega = W(t), \tag{8.22}$$

provided we put

$$R_{+-}(\omega,\omega) = \frac{1}{2\omega^2 H(\omega)}, \tag{8.23}$$

which is similar to a relation for $K_{+-}(\omega,\omega)$, derived in [10]. Indeed, it can be seen from (8.17) that the two conditions are consistent if and only if $k_{2+}(\omega,\omega) + k_{1-}(\omega,\omega) = 0$. Furthermore, if $R_{+-}(\omega_1,\omega_2)$ is replaced by an equivalent kernel, using the non-uniqueness arguments referred to after (8.17), then (8.23) is typically no longer valid.

From (5.45), $(8.14)_{2,3}$ and $(5.50)_4$, we obtain

$$\dot{\mathfrak{D}}(t) = D(t) = \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{I_{2F}^t(\omega_1)} R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2) d\omega_1 d\omega_2, \tag{8.24}$$

if

$$\frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{H(\omega_1) R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 + \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t(\omega_1)} R_{+-}(\omega_1,\omega_2) H(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 = 0. \tag{8.25}$$

The two terms on the left are complex conjugates of each other, and can be shown to be individually real, so that we can express this condition as

$$\frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{H(\omega_1) R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 = 0. \tag{8.26}$$

Let us apply (3.20) to the integral over ω_1 in (8.26). This gives, with the aid of (8.23) and $(5.50)_4$,

$$\begin{aligned}&\frac{i}{8\pi^2} P \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{H(\omega_1) R_{+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2 \\ &= -\frac{1}{8\pi} \int_{-\infty}^{\infty} H(\omega) R_{+-}(\omega,\omega) I_{2F}^t(\omega) d\omega \\ &= \frac{1}{16\pi} \int_{-\infty}^{\infty} I_F^t(\omega) d\omega\end{aligned} \tag{8.27}$$

It follows from $(8.19)_2$, (5.45) and (2.13) that

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$$\dot{\psi}(t) = -\frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\overline{I_{2F}^t}(\omega_1)R_{+-}(\omega_1,\omega_2)$$

$$I_{2F}^t(\omega_2)d\omega_1 d\omega_2 + \dot{E}(t)\Bigg[T_e(t) + \frac{i}{2\pi^2}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2\Bigg], \tag{8.28}$$

where the reality of the last integral has been invoked. Since (2.9) or $(7.12)_1$ must be satisfied, we require that

$$\frac{i}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2$$
$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} I_F^t(\omega)d\omega = [T(t) - T_e(t)]\dot{E}(t), \tag{8.29}$$

by virtue of (5.47). Now, using (3.19), we find that

$$\frac{i}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2$$
$$= \frac{i}{2\pi^2}P\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1 - \omega_2}d\omega_1 d\omega_2$$
$$+ \frac{1}{2\pi}\int_{-\infty}^{\infty} H(\omega)R_{+-}(\omega,\omega)I_{2F}^t(\omega)d\omega$$
$$= \frac{i}{2\pi^2}P\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1 - \omega_2}d\omega_1 d\omega_2$$
$$+ \frac{1}{4\pi}\int_{-\infty}^{\infty} I_F^t(\omega)d\omega. \tag{8.30}$$

Using (8.27), we see that (8.29) is satisfied.

Of the relations (8.23), (8.25) and (8.29), any two implies the third.

We can show directly that (8.29) is the frequency domain equivalent of (7.7). Using $(8.2)_1$ and (5.47), we can write (7.7) as

$$\frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\overline{G_+''}(\omega_1)L_{+-}(\omega_1,\omega_2)$$
$$I_{2+}^t(\omega_2)d\omega_1 d\omega_2 = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_F^t(\omega)d\omega. \tag{8.31}$$

With the help of (8.11), (8.12) and the property

$$\int_{-\infty}^{\infty} G_+''(\omega_1)L_{+-}(\omega_1,\omega_2)d\omega_1 = 0, \tag{8.32}$$

which follows by closing the integral on $\Omega^{(-)}$, we conclude from (3.5) that $\overline{G_+''}(\omega_1)$ can be replaced by $-2H(\omega_1)$. Also, we can replace I_{2+}^t by I_{2F}^t, as concluded in relation to (8.18). Thus, the left-hand side of (8.31) becomes

$$-\frac{1}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H(\omega_1)L_{+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)d\omega_1 d\omega_2$$
$$= \frac{i}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega_2)}{\omega_1^- - \omega_2^+}I_{2F}^t(\omega_2)d\omega_1 d\omega_2, \tag{8.33}$$

where (8.7) has been invoked. Therefore, (8.31) is equivalent to (8.29).

Similarly, we can show, using (8.9), that (8.26) is the frequency domain equivalent of (7.18).

We can write (8.29) in the form

$$\frac{1}{2\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H(\omega_1)L_{+-}(\omega_1,\omega_2)\omega_2^2$$
$$I_F^t(\omega_2)d\omega_1 d\omega_2 = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_F^t(\omega)d\omega, \tag{8.34}$$

with the aid of $(5.50)_4$.

Let us now explore possible solutions of (8.34), leading to new free energies. This equation must be true for an arbitrary history, so that, on using (5.44), we obtain the relations

$$\frac{1}{\pi}\int_{-\infty}^{\infty} H(\omega_1)L_{+-}(\omega_1,\omega)H(\omega)d\omega_1 = \frac{H(\omega)}{\omega^2} + S_-(\omega), \tag{8.35}$$

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where $S_{-}(\omega)$ is an arbitrary function that is analytic in Ω^{+} and goes to zero at infinity, since, by Cauchy's theorem,

$$\int_{-\infty}^{\infty} S_{-}(\omega)\overline{\dot{E}^t_{+}}(\omega)d\omega = 0. \tag{8.36}$$

Recall that (7.8) has the same relationship with (7.7) that (8.35) has with (8.34).

The frequency version of (7.11) has the same form as (8.35) and indeed (6.7). Comparing these latter two equations, we see that

$$\begin{aligned} \overline{f_{+}}(\omega) &= \frac{\omega}{\pi i}\int_{-\infty}^{\infty} H(\omega_1)L_{+-}(\omega_1,\omega)d\omega_1 - \frac{1}{i\omega^{+}} \\ &= -\frac{\omega}{\pi}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega)}{\omega_1-\omega^{+}}d\omega_1 - \frac{1}{i\omega^{+}}, \\ S_{-}(\omega) &= -\frac{1}{2}\overline{J_{+}}(\omega). \end{aligned} \tag{8.37}$$

Relations $(8.37)_{1,2}$ and (8.23) are constraints on $L_{+-}(\omega_1,\omega)$ and $R_{+-}(\omega_1,\omega)$, which derive from (7.11) or ultimately (2.16).

The quantity $f_{+}(\omega)$ is given by (6.9) for discrete spectrum materials, and is zero if the material has branch points.

Alternatively, we can argue that (8.26) must be true for arbitrary history $\overline{\dot{E}^t_{+}}(\omega)$, so that, instead of (8.35), we have

$$\frac{1}{i\pi}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega)H(\omega)}{\omega_1-\omega^{-}}d\omega_1 = S_{-}(\omega), \tag{8.38}$$

and $(8.37)_2$ is replaced by

$$\overline{f_{+}}(\omega) = -\frac{\omega}{\pi}\int_{-\infty}^{\infty}\frac{H(\omega_1)R_{+-}(\omega_1,\omega)}{\omega_1-\omega^{-}}d\omega_1. \tag{8.39}$$

Using (8.23), (3.19) and (3.20), we see that (8.39) is equivalent to $(8.37)_2$.

9 Quadratic forms for $\psi_f(t)$ in terms of I^t

Consider the quadratic forms (4.7) and (4.9). These can be replaced by quadratic forms in terms of $I^t_{2F}(\omega)$, using $(5.51)_1$. The question discussed in this section is: can they be expressed as quadratic forms in $I^t_{2+}(\omega)$, which would provide examples of $(8.14)_1$ and $(8.19)_1$ or, in the time domain, (7.1) and $(7.12)_2$. It emerges in Sect. 9.1 that only the minimum free energy $\psi_m(t)$ corresponding to $f = 1$ can be expressed in such a manner. This property of $\psi_m(t)$ is discussed in detail in Sect. 9.2.

This is consistent with the fact that $\psi_m(t)$ is a FMS. However, it is also true that all the $\psi_f(t)$ are FMSs. It will be shown how this property holds even though the $\psi_f(t)$ for $f > 1$ are not expressible as quadratic functionals of $I^t_{2+}(\omega)$ or in the time domain, $I^t_2(s)$, $s > 0$.

9.1 Quadratic forms for $\psi_f(t)$

We will base our discussion on (4.2) and (4.3). Referring to (4.3) and (5.51), we put

$$P^{ft}(\omega) = \frac{iH^f_{-}(\omega)}{\omega}\dot{E}^t_{+}(\omega) = \left[\frac{1}{2i\omega^{-}H^f_{+}(\omega)}\right]\left[\overline{I^t_{2F}}(\omega)\right]. \tag{9.1}$$

There is no singularity at $\omega = 0$ because of the factor ω^2 in $I^t_{2F}(\omega)$, given by $(5.50)_4$. The superscript on ω^{-} is chosen for convenience. The last form of P^{ft} is the product of two functions both in $L^2(\mathbb{R})$. For $f = 1$, the first factor has all its singularities in $\Omega^{(+)}$, by virtue of the property that the zeros of H^f_{+} are in $\Omega^{(+)}$. However, for other values of f, the zeros of H^f_{+} can be in $\Omega^{(+)}$ or $\Omega^{(-)}$. Using $(5.51)_2$, we obtain

$$P^{ft}(\omega) = \frac{1}{2i\omega^{-}H^f_{+}(\omega)}\left[\overline{I^t_{2+}}(\omega) + \overline{I^t_{2-}}(\omega)\right] \tag{9.2}$$

The quantity $p^{(ft)}_{-}(\omega)$ in (4.2) and (4.3) will now be considered in more detail. Let us write

$$\frac{1}{2i\omega^{-}H^f_{+}(\omega)} = A_{+}(\omega) + A_{-}(\omega), \tag{9.3}$$

where, as indicated by the notation, $A_{\pm}(\omega)$ has all its singularities in $\Omega^{(\pm)}$ respectively. For discrete spectrum materials, $H^f_{+}(\omega)$ is given by (4.20) and

$$\begin{aligned} \frac{1}{H^f_{+}(\omega)} &= \frac{1}{h_\infty} + \sum_{i=1}^{n}\frac{V^f_i}{\omega - i\rho^f_i}, \\ V^f_i &= \lim_{\omega\to i\rho^f_i}\frac{\omega - i\rho^f_i}{H^f_{+}(\omega)}, \quad i = 1,2,\ldots,n. \end{aligned} \tag{9.4}$$

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Thus, $2i\omega A_+(\omega)$ is equal to the sum of terms with $\rho_i^f = +\gamma_i$ and $2i\omega A_-(\omega)$ consists of terms where $\rho_i^f = -\gamma_i$.

If $f = 1$, then $A_-(\omega)$ will vanish, while for $f = N$ (yielding the maximum free energy referred to after (4.9); see also remark 7.1 of [10] and [1], p 343) $A_+(\omega)$ is zero. For all values of f, $p_\pm^{ft}(\omega)$ will be given by (4.3) with

$$P^{ft}(\omega') = A_+(\omega')\overline{I^t_{2+}}(\omega') + A_-(\omega')\overline{I^t_{2+}}(\omega') \\ +A_+(\omega')\overline{I^t_{2-}}(\omega') + A_-(\omega')\overline{I^t_{2-}}(\omega'). \tag{9.5}$$

The relation for $p_-^{(ft)}(\omega)$ can be simplified to give

$$p_-^{(ft)}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{A_+(\omega')\overline{I^t_{2+}}(\omega') + A_-(\omega')\overline{I^t_{2+}}(\omega') + A_-(\omega')\overline{I^t_{2-}}(\omega')}{\omega' - \omega^+} d\omega' \\ = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{A_+(\omega')\overline{I^t_{2+}}(\omega') + A_-(\omega')\overline{I^t_{2F}}(\omega')}{\omega' - \omega^+} d\omega'. \tag{9.6}$$

The first form follows by observing that if we evaluate the term with $A_+(\omega')\overline{I^t_{2-}}(\omega')$ by closing the contour on $\Omega^{(-)}$ then, by Cauchy's theorem, the result is zero.

Consider the second form. For the case of the minimum free energy, only the first term of the integrand is non-zero and it follows immediately that $\psi_m(t)$ can be expressed as a quadratic form in $I^t_{2+}(\omega)$, as noted above.

We now seek to show that $p_-^{(ft)}(\omega)$ (and therefore $\psi_f(t)$) is a FMS even if $f > 1$, for which the second term in the denominator of $(9.6)_2$ is non-zero. The argument will be presented for discrete spectrum materials (Remark 5.2) but is in fact more general.

The first term in $(9.6)_2$ contributes a sum of simple poles at the points $-i\alpha_l$, $l = 1, 2, \ldots, n$ by virtue of $(5.53)_2$, in an expression involving $\dot{E}^t_+(\omega)$ evaluated only at $\omega = -i\alpha_l$. This can be seen by closing the contour on $\Omega^{(-)}$. In the second term, the singularities of $A_-(\omega')$ are cancelled by $\overline{I^t_{2F}}(\omega')$ because of the factor $H(\omega')$ in this quantity, defined by (5.51). This can be shown by using (9.4) to evaluate $A_-(\omega)$, and by taking the product of $H^f_\pm(\omega)$, given by (4.20). The cancellation would not be manifest if $\overline{I^t_{2F}}$ were expressed in terms of $\overline{I^t_{2\pm}}$. Closing on $\Omega^{(-)}$ again, we find that the only contributing singularities are those at $-i\alpha_i$ in $H(\omega)$, in spite of the fact that $\overline{I^t_{2F}}$ is not a FMS. One again obtains an expression where the only dependence on $\dot{E}^t_+(\omega)$ is through $\dot{E}^t_+(-i\alpha_j)$, $j = 1, 2, \ldots, n$, as required by Remark 5.3.

However, the point we wish to emphasize here is that $p_-^{(ft)}$ for $f \neq 1$ or $f \neq N$ is linear in both $\overline{I^t_{2+}}$ and $\overline{I^t_{2F}}$, so that ψ_f is quadratic in these quantities, as we see from (4.2).

One could also have approached the above argument from another point of view, by expressing (4.7) as a quadratic functional in I^t_{2F}, using (5.51). With the aid of arguments similar to those after (9.6), one again obtains a quadratic functional of I^t_{2+} and I^t_{2F}. This approach is developed explicitly for the minimum free energy in Sect. 9.2.

These quadratic functionals can be expressed also in terms of time domain quantities, as shown for the minimum free energy in Sect. 9.2.

For $f = N$, giving the maximum free energy, the quadratic form depends only on I^t_{2F}.

Thus, for all linear combinations of the $\psi_f(t)$ involving terms with $f > 1$, we need to include $\overline{I^t_{2F}}$, and the property of being a FMS is dependent on a special cancellation, which is a specific property of the kernel associated with those given by (4.10), where at least one λ_f for $f > 1$ is non-zero. This will not necessarily hold for a quadratic form in I^t_{2+} and I^t_{2F} with a general kernel.

9.2 The minimum free energy as an explicit functional of I^t

It has already been shown in subsection 9.1 that the minimum free energy can be expressed as a quadratic form in $I^t_{2+}(\omega)$ or $I^t_2(\tau)$, $\tau \in \mathbb{R}^+$. Derivations of the explicit form of this functional were given in [1, 6]. We give a different derivation of this result here. Also, we show that the conditions (8.23) and (8.29) are obeyed.

Consider firstly the frequency domain representation. Recalling (5.51), we can write (4.7)–(4.9) (for $f = 1$, corresponding to the minimum free energy) in the form (after exchanging ω_1 and ω_2)

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$$\psi_m(t) = \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t}(\omega_1)R_{m+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2,$$
$$D_m(t) = \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I_{2F}^t}(\omega_1)R_{m+-}(\omega_1,\omega_2) I_{2F}^t(\omega_2)d\omega_1 d\omega_2,$$
$$\mathfrak{D}_m(t) = \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{I_{2F}^t(\omega_1)}R_{m+-}(\omega_1,\omega_2)I_{2F}^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2,$$
$$R_{m+-}(\omega_1,\omega_2) = \frac{1}{2\omega_1^- H_+(\omega_1)\omega_2^+ H_-(\omega_2)}. \tag{9.7}$$

The quantity $R_{m+-}(\omega_1,\omega_2)$ is analytic with respect to ω_1 in Ω^+ and with respect to ω_2 in Ω^-. We now replace I_{2F}^t in these two relations by the right-hand side of (5.51)$_2$. It follows from Cauchy's theorem, by closing the contour on $\Omega^{(+)}$, that

$$\int_{-\infty}^{\infty} \frac{R_{m+-}(\omega_1,\omega_2)I_{2-}^t(\omega_2)}{\omega_1^- - \omega_2} d\omega_2 = 0. \tag{9.8}$$

Similarly, $\overline{I_{2-}^t}(\omega_1)$ may be dropped from (9.7)$_1$ on integration over ω_1 and we obtain

$$\psi_m(t) = \phi(t) - \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\overline{I_{2+}^t}(\omega_1)R_{m+-}(\omega_1,\omega_2)I_{2+}^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2$$
$$= \phi(t) + \frac{1}{8\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I_{2+}^t}(\omega_1)L_{m+-}(\omega_1,\omega_2)I_{2+}^t(\omega_2)d\omega_1 d\omega_2,$$
$$L_{m+-}(\omega_1,\omega_2) = \frac{R_{m+-}(\omega_1,\omega_2)}{i(\omega_1^- - \omega_2^+)}, \tag{9.9}$$

which is the explicit quadratic form implied by (9.6) for $f = 1$. A similar argument yields that

$$D_m(t) = \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{I_{2+}^t}(\omega_1)R_{m+-}(\omega_1,\omega_2) I_{2+}^t(\omega_2)d\omega_1 d\omega_2$$
$$= \frac{1}{4\pi^2}\left|\int_{-\infty}^{\infty} \frac{I_{2+}^t(\omega)}{2\omega^+ H_-(\omega)} d\omega\right|^2 \tag{9.10}$$
$$= \frac{1}{4\pi^2}\left|\int_{-\infty}^{\infty} \frac{I_{2F}^t(\omega)}{2\omega H_-(\omega)} d\omega\right|^2.$$

Observe that (8.23) is true for (9.7)$_4$.

Consider now the time domain representations. We seek to express $D_m(t)$ and $\psi_m(t)$ as quadratic functionals of $I^t(s)$, $s \in \mathbb{R}^+$. Let us define the quantity $M(s)$ by

$$M(s) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{1}{2i\omega^- H_+(\omega)} e^{i\omega s} d\omega, \quad s \in \mathbb{R}. \tag{9.11}$$

This is a real quantity which vanishes for $s \in \mathbb{R}^{--}$. The integrand has a quadratic singularity near the origin, due to the explicit pole term and the factor ω in $H_+(\omega)$ which is taken, for consistency, to be ω^-. This gives a finite contribution.

Let us write the time domain version of (9.9)$_2$ in the form

$$\psi_m(t) = \phi(t) + \frac{1}{2}\int_0^{\infty}\int_0^{\infty} I_2^t(u)L_m(u,v)I_2^t(v)dudv, \tag{9.12}$$

corresponding to (7.1), where $L_m(u,v)$ is given by (8.2)$_1$ in terms of $L_{+-}(\omega_1,\omega_2)$. The rate of dissipation given by (9.10) becomes, in the time domain, (*c.f.* (4.6))

$$D_m(t) = |K(t)|^2, \quad K(t) = \int_0^{\infty} M(u)I_2^t(u)du, \tag{9.13}$$

on using Parseval's formula. Therefore

$$D_m(t) = \left|\int_0^{\infty} M(u)I_2^t(u)du\right|^2$$
$$= \int_0^{\infty}\int_0^{\infty} I_2^t(u)M(u)M(v)I_2^t(v)dudv, \tag{9.14}$$

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so that

$$R(s,u) = 2M(s)M(u). \tag{9.15}$$

It follows from (7.28) that

$$L_m(u,v) = 2\int_0^{\min(u,v)} M(u-z)M(v-z)dz = L_m(v,u). \tag{9.16}$$

The following two results are of interest.

Proposition 9.1 We seek to show that $(8.29)_1$ holds for the minimum free energy. This implies that the equivalent time domain version (7.7) is also true.

Proof Substitute $R_{m+-}(\omega_1,\omega_2)$, given by $(9.7)_4$, into the left-hand side of (8.29). By integrating around $\Omega^{(+)}$, we obtain

$$\frac{i}{2\pi^2}\int_{-\infty}^{\infty}\frac{H_-(\omega_1)}{\omega_1(\omega_1-\omega_2^+)}d\omega_1 = -\frac{1}{\pi}\frac{H_-(\omega_2)}{\omega_2}, \tag{9.17}$$

and $(8.29)_1$ follows immediately, on noting the last relation of (5.50). □

Proposition 9.2 The quantity $\overline{f_+}(\omega)$ in (8.37) or (8.39) vanishes in the case of the minimum free energy

Proof For (8.39), closing the ω_1 contour over $\Omega^{(+)}$ gives zero. For $(8.37)_2$, the two terms cancel. □

Thus, this property, which is true for all free energies in materials with branch cut singularities, holds also for materials with only isolated singularities in the case of the minimum free energy.

Proposition 9.3 The minimum free energy is the only free energy functional for which the rate of dissipation is given by a simple product. This is in effect the result that the factorization of $H(\omega)$, given by (3.8) and (3.9), where both zeros and singularities of $H_\pm(\omega)$ are in $\Omega^\pm$ respectively, is unique up to a sign ([1], p 240).

Proof Let

$$R_{+-}(\omega_1,\omega_2) = r_+(\omega_1)r_-(\omega_2), \tag{9.18}$$

under the condition

$$|r_+(\omega)|^2 = \frac{1}{2\omega^2 H(\omega)}. \tag{9.19}$$

Equation (8.39) reduces to

$$\int_{-\infty}^{\infty}\frac{H(\omega_1)r_+(\omega_1)}{\omega_1-\omega^-}d\omega_1 = -\frac{\overline{f_+}(\omega)\pi}{\omega r_-(\omega)} = F_-(\omega), \tag{9.20}$$

since the zeros of $r_-(\omega)$ are in $\Omega^{(-)}$. Using the Plemelj formulae (3.19) and (3.20), we can write (*cf.* (4.3))

$$\begin{aligned} &H(\omega_1)r_+(\omega_1) = \rho_-(\omega_1) - \rho_+(\omega_1),\\ &\rho_\pm(\omega_1) = \frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{H(\omega_1)r_+(\omega_1)}{\omega_1-\omega^\mp}d\omega_1, \end{aligned} \tag{9.21}$$

and (9.20) is the requirement that $\rho_+(\omega) = F_-(\omega)$. Both sides vanish at infinity, so that both must be zero everywhere, by Liouville's theorem (for example, [1], p 534). Thus, we have that

$$H_+(\omega_1)r_+(\omega_1) = \frac{\rho_-(\omega_1)}{H_-(\omega_1)}. \tag{9.22}$$

Multiplying across by a factor ω_1, we see that both sides must be equal to a constant k, by Liouville's theorem, giving

$$r_+(\omega_1) = \frac{k}{\omega H_+(\omega_1)}. \tag{9.23}$$

It follows from (9.19) that $|k|^2 = 1/2$, and (9.23), substituted into (9.18), yields $(9.7)_4$. Thus, the minimum free energy is the only possibility associated with (9.18). The requirement that $F_-(\omega)$ vanishes implies that, in agreement with proposition 9.2, we have $\overline{f_+}(\omega) = 0$. □

10 General form of free energies that are FMSs: discrete spectrum materials

We now present quadratic forms in terms of the minimal state functionals I^t for discrete spectrum materials, just as (5.25) and (5.28) apply to quadratic forms in terms of histories. Let us consider the form $(8.14)_1$ for $I^t_{2+}(\omega)$ given by $(5.53)_2$. We obtain

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$$
\begin{aligned}
D(t) &= \frac{1}{2}\mathbf{w}^{\top}(t)\mathbf{R}\mathbf{w}(t)\\
\mathbf{w}(t) &= (w_1(t), w_2(t), \ldots, w_n(t)), \quad w_i(t) = \alpha_i^2 G_i e_i(t),\\
R_{ij} &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{R_{+-}(\omega_1,\omega_2)}{(\omega_1+i\alpha_i)(\omega_2-i\alpha_j)}d\omega_1 d\omega_2\\
&= R_{+-}(-i\alpha_i, i\alpha_j), \quad i,j = 1,2,\ldots,n,
\end{aligned}
\tag{10.1}
$$

where $e_i(t)$ is defined by (5.24) and the last relation is deduced by integrating over $\Omega^{(-)}$ on the ω_1 plane and $\Omega^{(+)}$ on the ω_2 plane. Relations (10.1) can also be obtained from (7.12) and (5.52).

The free energy functional (7.1) has the form

$$
\begin{aligned}
\psi(t) &= \phi(t) + \frac{1}{2}\mathbf{w}^{\top}(t)\mathbf{L}\mathbf{w}(t)\\
L_{ij} &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{L_{+-}(\omega_1,\omega_2)}{(\omega_1+i\alpha_i)(\omega_2-i\alpha_j)}d\omega_1 d\omega_2\\
&= L_{+-}(-i\alpha_i, i\alpha_j) = \frac{R_{ij}}{\alpha_i+\alpha_j}, \quad i,j = 1,2,\ldots,n,
\end{aligned}
\tag{10.2}
$$

by virtue of (8.7). The quantities $\mathbf{R}$ and $\mathbf{L}$ are symmetric. Using (5.27), we see that

$$
\begin{aligned}
\dot{w}_i(t) &= -\alpha_i w_i(t) + z_i \dot{E}(t),\\
z_i &= \alpha_i^2 G_i, \quad i = 1,2,\ldots,n.
\end{aligned}
\tag{10.3}
$$

It follows that (2.9) holds, provided that

$$
\sum_{i=1}^{n}\frac{w_i(t)}{\alpha_i^2}\left[1 - \sum_{j=1}^{n}\alpha_i^2 L_{ij}\alpha_j^2 G_j\right] = 0, \tag{10.4}
$$

which is (7.7) for discrete spectrum materials. Let us put

$$
L_{ij} = \frac{l_{ij}}{\alpha_i^2\alpha_j^2}, \quad i,j = 1,2,\ldots,n, \tag{10.5}
$$

in terms of the matrix $\mathbf{l}$. Relation (10.4) holds for all histories, so that we must have

$$
\sum_{j=1}^{n} l_{ij} G_j = 1, \quad i = 1,2,\ldots,n. \tag{10.6}
$$

Referring to (5.26), we see that if $\mathbf{l} = \mathbf{C}^{-1}$, then (10.6) holds. The form (10.6) corresponds to the Laplace transform of $(7.11)_3$ for discrete spectrum materials, at the points $i\alpha_i$, where, from (6.9), we know that $\overline{f_+}(i\alpha_i) = 0,\ i = 1,2,\ldots,n.$

We can also see that $(8.37)_1$ gives

$$
\begin{aligned}
\overline{f_+}(\omega) &= i\omega\sum_{i=1}^{n}\alpha_i^2 G_i L_{+-}(-i\alpha_j,\omega) - \frac{1}{i\omega^+}\\
&= -\omega\sum_{i=1}^{n}\frac{\alpha_i^2 G_i R_{+-}(-i\alpha_j,\omega)}{\omega+i\alpha_i} - \frac{1}{i\omega^+}
\end{aligned}
\tag{10.7}
$$

on using $(4.14)_2$, (8.12) and by closing the contour on $\Omega^{(-)}$. Putting $\omega = i\alpha_j$ yields (10.6).

The expressions (10.1) and (10.2) are not helpful in characterizing quadratic forms in terms of $I_2^t(s),\ s \in \mathbb{R}^+$ because they are, in effect, quadratic forms in the $e_i(t)$; while the free energies ψ^f, given by (4.7), and discussed in Sect. 9, can also be expressed as such quadratic forms, even though they depend on $\overline{I_{2F}^t}(\omega)$ in the frequency domain, or $I_2^t(s),\ s \in \mathbb{R}$, in the time domain.

11 Proof that no new free energies can be expressed in terms of I^t

The approach adopted in [10] was based on product formulae in the time domain, and more particularly in the frequency domain, for the kernel of the rate of dissipation, which ensure that this quantity is non-negative. They also ensure that the resulting free energy has the correct non-negativity properties. In principle, the same approach should apply in the present context, as demonstrated in Sect. 7.1. However, as we will now show, there are no free energy functionals expressible as quadratic forms in I^t other than the minimum free energy. This is a generalization of the conclusion of Sect. 9.1 that, of the family $\psi_f(t)$, only $\psi_m(t)$ has this property. It further indicates how restrictive the requirement is that a free energy functional be expressible in the form (7.1) or $(8.18)_1$.

Proposition 11.1 The only possible choice of $L_{+-}(\omega_1,\omega_2)$ obeying (8.37) is the kernel $L_{m+-}(\omega_1,\omega_2)$, given by $(9.9)_3$.

Proof We express $L_{+-}(\omega_1,\omega_2)$ in the form

$$
L_{+-}(\omega_1,\omega_2) = L_{m+-}(\omega_1,\omega_2) + L_{1+-}(\omega_1,\omega_2). \tag{11.1}
$$

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The case of materials with only discrete spectrum singularities (remark 5.2) will be considered first. The quantity $L_{m+-}(\omega_1,\omega_2)$ is a solution of (8.37)$_{1,2}$ for $\overline{f_+}(\omega)=0$ (proposition 9.2), so that we have

$$\begin{aligned}
\overline{f_+}(\omega) &= U(\omega),\\
U(\omega) &= \frac{\omega}{\pi i}\int_{-\infty}^{\infty} H(\omega_1)L_{1+-}(\omega_1,\omega)d\omega_1\\
&= \frac{\omega}{\pi i}\int_{-\infty}^{\infty} H_+(\omega_1)H_-(\omega_1)L_{1+-}(\omega_1,\omega)d\omega_1,\\
&\quad \forall\omega\in\mathbb{R}.
\end{aligned}\tag{11.2}$$

The quantity $f_+(\omega)$ is given by (6.9); it vanishes at $-i\alpha_i$, $i=1,2,\ldots,n$, and has singularities at $i\chi_i$, $i=0,1,\ldots,n$, where the parameters χ_i are arbitrary positive quantities. The kernel $L_{1+-}(\omega_1,\omega)$ must depend on the χ_i, since $H(\omega_1)$ is independent of them. Let us seek forms of $L_{1+-}(\cdot,\cdot)$ which are solutions of (11.2)$_1$, for any choices of the χ_i.

The simplest way of ensuring that the zeros of $U(\omega)$ are consistent with the location of the zeros of $\overline{f_+}(\omega)$ is to assume that $L_{1+-}(\omega_1,\omega)$ vanishes at each point $\omega=i\alpha_i$. Alternatively, if $L_{1+-}(\omega_1,\omega)$ is not zero at a given point $\omega=i\alpha_i$, then it is still possible that $U(i\alpha_i)$ could vanish, for given values of χ_i, thus achieving consistency with (11.2)$_1$. Thus, we take the quantity $L_{1+-}(\omega_1,\omega)$ to be zero at each point $\omega=i\alpha_i$ for most values of the parameters χ_i, $i=1,2,\ldots,n$.

Let us consider a given set of values χ_j, $j\neq k$ as fixed parameters, and regard $U(\omega)$ as a function of χ_k, denoted by $U(\omega,\chi_k)$. Now, $U(i\alpha_i,\chi_k)$ may have discrete roots, in other words, may vanish at discrete values of χ_k. However, this does not allow us to drop the assumption that $L_{1+-}(\omega_1,i\alpha_i)$ is zero at these values of χ_k, since such an assumption would introduce anomalous discontinuities in the function $L_{1+-}(\omega_1,i\alpha_i)$, regarded as a function of χ_k, because it is zero for almost all choices of this parameter and non-zero at certain isolated values.

It follows that $L_{1+-}(\omega_1,\omega)$ must be taken to vanish at each point $\omega=i\alpha_i$, $i=1,2,\ldots,n$. Relation (8.3) then implies that it is zero at each point $\omega_1=-i\alpha_i$, $i=1,2,\ldots,n$, and the singularities of $H_-(\omega_1)$, as given by (4.18)$_3$, are cancelled by $L_{1+-}(\omega_1,\omega)$ in (11.2)$_3$. The remaining singularities of the integrand are all in $\Omega^{(+)}$. Therefore, by closing the contour on $\Omega^{(-)}$ and recalling (8.11), we find that the right-hand side of (11.2) vanishes.

Thus, there are no kernels that are consistent with a non-zero choice of $f_+(\omega)$. Any acceptable choice of $L_{1+-}(\omega_1,\omega)$ must obey the equation

$$\int_{-\infty}^{\infty} H_+(\omega_1)H_-(\omega_1)L_{1+-}(\omega_1,\omega)d\omega_1=0,\quad \forall\omega\in\mathbb{R}.\tag{11.3}$$

The only way to ensure this condition for all ω is to assign to $L_{1+-}(\omega_1,\omega)$ the property that it vanishes at each point $\omega_1=-i\alpha_i$, and thereby cancels the singularities in $H_-(\omega_1)$. But these points are the singularities of $\overline{I_{2+}^t}(\omega_1)$ in (8.18), so that the quadratic form with kernel $L_{1+-}(\omega_1,\omega)$ would give a zero contribution to the free energy, as can be seen by integrating ω_1 over a contour on $\Omega^{(-)}$.

We conclude that $f_+(\omega)$ must be zero, even for materials with only isolated singularities and $L_{1+-}(\omega_1,\omega)$ in (11.1) makes no contribution to the free energy functional.

For materials with some branch cuts, the quantity $f_+(\omega)$ vanishes, in any case, and we must have a relation of the same form as (11.3). Then, there will be some branch cuts in $L_{1+-}(\omega_1,\omega)$ as a function of ω_1. These must be in $\Omega^{(+)}$. There will also be branch cuts in $H_-(\omega_1)$, which must be in $\Omega^{(-)}$. There is no mechanism whereby these can neutralize or cancel each other. The only remaining possibility is that $L_{1+-}(\omega_1,\omega)$ vanishes. □

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