



Constructing Free Energies for Materials with Memory

We now discuss methods for deriving new functionals which have the properties of a free energy. Perhaps the central difficulty in constructing such quantities arises in making choices that ensure both a nonnegative quadratic form for the free energy and the rate of dissipation. Typically, if one chooses a suitable functional for the free energy, the associated rate of dissipation does not have the non-negativity property. A technique is presented in this chapter (see also [162]) which in effect reverses this procedure. We choose a nonnegative functional for the rate of dissipation and derive formulae which give the associated free energy functional in terms of the dissipation rate kernel. It emerges that the resulting free energy has the required non-negativity property.

The main topics dealt with in this chapter are based on [162] and are a development of the discussion in Sect. 7.1.3. Also, Sects. 17.1 and 17.6 are based on results in [18].

Also discussed in this chapter is the issue of approximating a general discrete-spectrum relaxation function by a relaxation function with one decaying exponential, corresponding to the Day free energy.

Finally, we consider single-integral free energies in terms of the functional I' , which is the functional of the minimal state defined by (16.5.1).

17.1 Two Equivalent Interpretations of the Set of Free Energies

Before deriving the main results of this chapter, we discuss two possible interpretations of the set of free energy functionals associated with a given constitutive equation relating stress and strain.

Let us identify a particular material with memory, which will be referred to as material I. It is assumed to exhibit linear behavior. The stress-strain or constitutive relation of this material is known, in other words, its relaxation function is given. There are generally many free energies and corresponding dissipation functionals

associated with material I. All of these generate the same stress and therefore have the same relaxation function. As in earlier chapters, we denote this convex set by \mathcal{F} , which is of course dependent on the choice of strain history. The physical free energy for material I, yielding the observed rate of dissipation, is a member of \mathcal{F} , as well as all free energies generating the given stress.

It is shown in [162, 164] (see also Sect. 17.2) that any material with memory can be uniquely characterized by specifying the kernel of its physical rate of dissipation functional. This quantity determines the associated free energy kernel and the relaxation function, which in turn yields the stress-strain or constitutive relation, for a given strain history. The work function can be deduced from these quantities. Also, the dissipation kernel determines the amount of dissipation under deformation. We will consider the set of all such kernels associated with materials with a specified constitutive relation; this set will be denoted by \mathcal{K} . For a given choice of strain history, \mathcal{K} generates a set of free energies \mathcal{F} , corresponding to our chosen constitutive relation. It will emerge that the boundaries of \mathcal{K} and \mathcal{F} are at least roughly determined by the relaxation function of the constitutive relation.

The following alternative viewpoint is now described. We interpret the set of kernels \mathcal{K} as specifying all the distinct linear materials with the same constitutive relation but different dissipation rates as a result of deformation. These can be labeled by individual members of \mathcal{K} . One of them yields the physical free energy in \mathcal{F} for material I. Other members of \mathcal{F} would traditionally be regarded as approximations to or bounds on (notably the minimum and maximum free energy) this physical free energy. Instead, we now regard these, or more specifically the corresponding kernels in \mathcal{K} , as describing different actual materials with the same constitutive relation, but different dissipation properties. For the material labeled by a particular kernel, the relevant member of \mathcal{F} for a given strain history is the physical free energy for that material. Particular examples may not currently exist as real materials but it seems reasonable to assume that they could be manufactured, to a close approximation, now or in the future.

Both of the above viewpoints are valid and can be adopted as context demands. We will refer to the more traditional viewpoint, where \mathcal{K} is the set of kernels producing the physical free energy of material I as well as approximations to and bounds on this quantity, as Interpretation I or I1. The viewpoint that each $K(s, u) \in \mathcal{K}$ fully describes a separate material, each equally of interest and with the same constitutive equation, will be referred to as I2.

Under I2, the set \mathcal{K} is defined not by the choice of material I but by the constitutive equation of the materials. If we replace material I by another material with the same stress-strain relation, the set \mathcal{K} remains unchanged. We do not focus on one specific example but rather treat all materials labeled by members of \mathcal{K} on an equal footing.

The Day free energy, a discrete-spectrum material with one decay time, is the only free energy that is a functional of the minimal state. It is therefore the unique physical free energy for that material. This quantity and the associated dissipation are explored for a choice of relaxation function approximately equal to that for the more general set of materials under consideration.

17.2 Unique Characterization of Materials with Memory

Materials with linear memory constitutive relations, i.e., a linear functional of the strain history, are characterized by a relaxation function, if we leave aside the matter of stored and dissipated energy. Following the discussion in Sects. 7.1.3 and 17.1, it is proposed that a material is characterized by the kernel of the rate of dissipation functional. This will be shown to yield a unique free energy and relaxation function. It also answers the question posed in Sect. 7.1.3 about two alternatives, by choosing the second option, though the first option remains of interest since all free energies obtained to date are examples of this.

There are generally many rates of dissipation and free energy kernels which yield a given relaxation function. Such non-uniqueness means that there is no simple method of identifying which is the physical free energy and rate of dissipation of a particular material. Ideally, the behavior of this kernel should be determined by measurements carried out on the material of interest, in which case it would be the physical kernel. This would lead to a unique, valid, free energy and provides a formula for the relaxation function. Thus, it is a complete characterization of the material. Of course, we are not referring to a real material, but rather a mathematical model, approximately describing some aspects of the behavior of a real material.

The kernel of the rate of dissipation functional is, however, difficult to measure, particularly in a non-isothermal context. For an isothermal problem, a quadratic functional using this kernel is the amount of heat produced per unit time by work on the material. The issue of measurement is briefly discussed in Sect. 7.1.3.

The standard approach to determining free energy functionals is to specify the relaxation function and seek free energy functionals either explicitly dependent on this quantity, or through a factorization process on a function derivable from it (see option 1 in Sect. 7.1.3). The first method is applicable only if this relaxation function is a monotonically decaying quantity, while the second approach yields the minimum and related free energies, which lie on the boundaries of \mathcal{F} . However, since we generally cannot determine the physically correct choice, this approach provides a complete description of constitutive behavior in the sense of stress-strain relations, but gives at best a partial characterization of energy storage and dissipation.

Our assertion is that a material with memory should be characterized by the kernel of the rate of dissipation, $K(\cdot, \cdot)$, defined in (17.3.12). Using a simple formula, the kernel of a unique free energy, $\widetilde{G}(\cdot, \cdot)$, with the correct non-negativity property, can then be deduced, from which in turn the relaxation function can be obtained.

It is assumed that, as a separate exercise, the equilibrium free energy has been fully determined. For completely linear materials, as given by (16.1.32) and (16.1.6), this amounts to measuring G_∞ , which is part of the task of determining the relaxation function.

Thus, all properties of the material are uniquely defined.

These developments are discussed in Sects. 17.4 and 17.5; see also [164].

17.3 Quadratic Models for Free Energies

Materials with linear constitutive relations will have free energies that are quadratic functionals. Let us first consider the simplest models for such materials.

17.3.1 A Single-Integral Model

Consider the form

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty C(s)[E_r^t(s)]^2 ds. \quad (17.3.1)$$

The integral term in (17.3.1) must be nonnegative for all histories by virtue of condition P2 or (16.1.26) of the Grafti conditions, which requires that $C(s)$ be a nonnegative quantity for all $s \in \mathbb{R}^+$. If (16.1.25) is to yield the constitutive relations (16.1.3)₁ for any arbitrary choice of history of strain, we must put $C(s) = -G'(s)$ where $G'(s)$ is assumed to be nonnegative, giving

$$\begin{aligned} \psi(t) &= \phi(t) - \frac{1}{2} \int_0^\infty G'(s)[E_r^t(s)]^2 ds \\ &= S(t) - \frac{1}{2} \int_0^\infty G'(s)[E^t(s)]^2 ds, \end{aligned} \quad (17.3.2)$$

$$S(t) = \phi(t) + (T(t) - T_0(t))E(t) + \frac{1}{2}(G_0 - G_\infty)E^2(t).$$

The quantity $S(t)$ is the quantity defined by (7.1.19)₂, modified in the manner specified before (7.1.35), for scalar theories. The rate of dissipation associated with ψ can be determined from (16.1.28) to have the form

$$D(t) = \frac{1}{2} \int_0^\infty G''(s)[E_r^t(s)]^2 ds \geq 0, \quad (17.3.3)$$

provided it is assumed that $G''(s) \geq 0$, $\forall s \in \mathbb{R}^+$. We conclude that there is only one example of a single-integral quadratic free energy in terms of strain history and this quantity is a free energy only if the conditions

$$G'(s) \leq 0, \quad G''(s) \geq 0, \quad \forall s \in \mathbb{R}^+ \quad (17.3.4)$$

hold. This is of course the Grafti–Volterra free energy functional discussed in Sect. 10.1.1.

Remark 17.3.1. The first condition in (17.3.4) yields the non-negativity of the integral term in the free energy and ensures that Grafti condition P2 is satisfied, while the second condition relates to P3, ensuring that the rate of dissipation is nonnegative or the second law holds. The second condition implies the first condition, as can be seen from the relation

$$G'(s) = - \int_s^\infty G''(u) du.$$

However, the first condition does not in general imply the second. Thus, for functional forms which are free energies only for materials obeying (17.3.4), the requirement that the rate of dissipation be nonnegative is sufficient to ensure the nonnegativity of the free energy, but not *vice-versa*. This is not surprising since P2 actually follows from P3 [67].

17.3.2 A Double Integral Model

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

$$\begin{aligned}
 \psi(t) &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \mathfrak{G}(s, u) E_r^t(u) ds du \\
 &= S(t) + \frac{1}{2} \int_0^\infty \int_0^\infty E^t(s) \mathfrak{G}(s, u) E^t(u) ds du \\
 &= \phi(t) - \phi_l(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) G(s, u) \dot{E}^t(u) ds du \quad (17.3.5) \\
 &= \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) \tilde{G}(s, u) \dot{E}^t(u) ds du, \\
 \mathfrak{G}(s, u) &= \frac{\partial^2}{\partial s \partial u} G(s, u) = G_{12}(s, u), \quad \tilde{G}(s, u) = G(s, u) - G_\infty,
 \end{aligned}$$

where $S(t)$ is defined by (17.3.2)₃, $\phi_l(t)$ by (16.1.32) and $T_0(t)$ by (16.1.3)₅. This is the scalar version of the full tensor developments of Sect. 7.1. There is no loss of generality in taking

$$\tilde{G}(s, u) = \tilde{G}(u, s), \quad \mathfrak{G}(s, u) = \mathfrak{G}(u, s). \quad (17.3.6)$$

The following properties of G will be assumed to hold for $s, u \in \mathbb{R}^+$:

$$\begin{aligned}
 G_\infty &= G(\infty, u) = G(s, \infty), \\
 G_1(s, \infty) &= G_2(\infty, u) = 0, \\
 G_1(\infty, s) &= G_2(u, \infty) = 0 \quad \forall s, u \in \mathbb{R}^+.
 \end{aligned} \quad (17.3.7)$$

Furthermore, we have

$$G_0 = G(0, 0). \quad (17.3.8)$$

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

$$G(u) = G(0, u) = G(u, 0) \quad \forall u \in \mathbb{R}^+, \quad (17.3.9)$$

yielding

$$G'(u) = G_2(0, u) = G_1(u, 0). \quad (17.3.10)$$

Relation (17.3.9) is the basic constraint ensuring that (16.1.25) holds. Conversely, if (16.1.25) is valid for all histories, then (17.3.9) must be true.

Relation (17.3.7)_{1,2} for $s = u = 0$ and (17.3.8) agree with (16.1.4), by virtue of (17.3.9). The Gaffi condition P2, given by (16.1.26), requires that the kernels \mathfrak{G} and \tilde{G} must be such that the integral terms in (17.3.5)_{1,4} are nonnegative.

Remark 17.3.2. We will consider all free energies associated with a given constitutive equation. Thus, the quantity $G(u)$ is the same for all choices of free energy, *i.e.*, for all choices of $G(s, u)$.

Referring to the quantity $S(t)$ in (17.3.2) and (17.3.5)₂, we see that

$$\frac{\partial}{\partial E(t)} S(t) = T(t),$$

which is condition P1 or (16.1.25).

The rate of dissipation can be deduced from (16.1.28) and (16.1.3)_{10,11} to be

$$\begin{aligned} D(t) &= -\frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) K(s, u) \dot{E}^t(u) ds du \\ &= -\frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \mathcal{K}(s, u) E_r^t(u) ds du, \end{aligned} \tag{17.3.11}$$

where

$$K(s, u) = G_1(s, u) + G_2(s, u), \quad \mathcal{K}(s, u) = \mathfrak{G}_1(s, u) + \mathfrak{G}_2(s, u). \tag{17.3.12}$$

The quantity G must be such that the integral in (17.3.11) is non-positive, as required by P3 of the Grafti conditions. We have

$$\mathcal{K}(s, u) = \frac{\partial^2}{\partial s \partial u} K(s, u) = K_{12}(s, u). \tag{17.3.13}$$

The quantities K and \mathcal{K} can also be taken to be symmetric in their arguments, *i.e.*,

$$K(s, u) = K(u, s), \quad \mathcal{K}(s, u) = \mathcal{K}(u, s). \tag{17.3.14}$$

The non-negativity requirements on \tilde{G} , \mathfrak{G} , $-K$, and $-\mathcal{K}$ imply in particular that

$$\begin{aligned} \tilde{G}(s, s) &\geq 0, & \mathfrak{G}(s, s) &\geq 0, \\ K(s, s) &\leq 0, & \mathcal{K}(s, s) &\leq 0, \quad s \in \mathbb{R}^+. \end{aligned} \tag{17.3.15}$$

In the approach developed in this chapter, the quantity $K(s, u)$ will play a more fundamental role than $G(s, u)$.

Seeking to express $\mathcal{D}(t)$ given by (16.1.30)₂ as a general quadratic functional form similar to those in (17.3.5) or (17.3.11), we put

$$\begin{aligned} \mathcal{D}(t) &= \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) Q(s, u) \dot{E}^t(u) ds du \\ &= \frac{1}{2} \int_0^\infty \int_0^\infty E_r^t(s) \mathfrak{Q}(s, u) E_r^t(u) ds du. \end{aligned} \tag{17.3.16}$$

There are two equivalent alternatives for the developments outlined below, the first being to use $\tilde{G}(s, u)$, $K(s, u)$, $\dot{E}^t(s)$ and the second to use $\mathfrak{G}(s, u)$, $\mathcal{K}(s, u)$, $E_r^t(s)$. Both have been widely adopted in discussing the minimum and related free energies. The first approach will be favored in the present context, though in earlier chapters, the other formulation is widely used, so there is a need to move between the two notations.

Remark 17.3.3. The Principle of Causality must apply to all physical systems and in the present context means that quantities such as $T(t)$, $\psi(t)$, $D(t)$, etc. can only depend on $E(s)$, $s \leq t$. Therefore, we can write (16.1.3)₄ and (17.3.5)₄, for example, in the form

$$\begin{aligned} T(t) &= T_e(t) + \int_{-\infty}^{\infty} \widetilde{G}(s) \dot{E}^t(s) ds, \\ \psi(t) &= \phi(t) + \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dot{E}^t(s) \widetilde{G}(s, u) \dot{E}^t(u) ds du, \end{aligned}$$

provided that

$$\dot{E}^t(s) \widetilde{G}(s, u) \dot{E}^t(u) = 0, \quad s, u < 0, \quad \widetilde{G}(s) \dot{E}^t(s) = 0, \quad s < 0. \quad (17.3.17)$$

The simplest way to enforce (17.3.17) is to take either option (a) or (b), given by

$$\begin{aligned} (a) \quad & \dot{E}^t(s) = 0, \quad \widetilde{G}(s, u), \widetilde{G}(s) \text{ arbitrary, for } s, u < 0; \\ (b) \quad & \widetilde{G}(s, u), \widetilde{G}(s) = 0, \quad \dot{E}^t(s) \text{ arbitrary, for } s, u < 0. \end{aligned} \quad (17.3.18)$$

The arbitrariness of $\widetilde{G}(\cdot, \cdot)$, $\widetilde{G}(\cdot)$, and $E^t(\cdot)$ for negative arguments is subject to the requirement that certain integrals of these quantities (for example, Fourier transforms) converge.

17.3.3 The Work Function

This quantity, given by (16.1.30)₁, can be put in the following forms (see Sect. 7.5):

$$\begin{aligned} W(t) &= \phi(t) + \frac{1}{2} \int_0^{\infty} \int_0^{\infty} \dot{E}^t(s) \widetilde{G}(|s - u|) \dot{E}^t(u) ds du \\ &= \phi(t) + \frac{1}{2} \int_0^{\infty} \int_0^{\infty} E_r^t(s) \frac{\partial^2}{\partial s \partial u} G(|s - u|) E_r^t(u) ds du \\ &= \phi(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} |\dot{E}_+^t(\omega)|^2 d\omega \\ &= \phi(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} H(\omega) |E_{r+}^t(\omega)|^2 d\omega. \end{aligned} \quad (17.3.19)$$

Both versions of the frequency domain formulation are manifestly nonnegative. One follows from the other by invoking (16.1.17). We see that it can be cast in the forms (17.3.5)_{1,4} by putting

$$\widetilde{G}(s, u) = \widetilde{G}(|s - u|), \quad G_{12}(s, u) = \frac{\partial^2}{\partial s \partial u} G(|s - u|). \quad (17.3.20)$$

Remark 17.3.4. The quantity $W(t)$ can be formally regarded as a free energy, but with zero dissipation, which is clear from (16.1.29). 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 (16.1.29) for any free energy $\psi(t)$. Indeed, we have in general the requirement that

$$\psi(t) \leq W(t). \quad (17.3.21)$$

A problem with the treatment of $W(t)$ as a free energy is raised in Chap. 18.

From (16.1.29), (17.3.16), (17.3.19) and (17.3.20), we deduce that

$$\begin{aligned} Q(s, u) &= \tilde{G}(|s - u|) - \tilde{G}(s, u), \\ Q(s, u) &= G_{12}(|s - u|) - \mathcal{G}(s, u), \end{aligned} \quad (17.3.22)$$

from which it follows that

$$\begin{aligned} Q_1(s, u) + Q_2(s, u) &= -G_1(s, u) - G_2(s, u) = -K(s, u), \\ Q_1(s, u) + Q_2(s, u) &= -\mathcal{G}_1(s, u) - \mathcal{G}_2(s, u) = -\mathcal{K}(s, u). \end{aligned} \quad (17.3.23)$$

Relations (17.3.22) also yield

$$Q(s, 0) = Q(0, u) = 0 \quad \forall s, u \in \mathbb{R}^+, \quad (17.3.24)$$

and

$$\int_0^\infty Q(s, v)dv = \int_0^\infty Q(v, u)dv = 0 \quad \forall s, u \in \mathbb{R}^+, \quad (17.3.25)$$

by virtue of (17.3.7), (17.3.9) and (17.3.10). A consequence of (17.3.25) is that (17.3.16)₂ can be replaced by

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

A requirement similar to (17.3.15) must be imposed on Q . In the light of (17.3.22)₁, we have

$$Q(s, s) = \tilde{G}_0 - \tilde{G}(s, s) = G_0 - G(s, s) \geq 0, \quad \forall s \in \mathbb{R}^+.$$

The corresponding relation for Q presents difficulties in that the quantities involved have a delta function singularity, which arises from the differentiations in (17.3.22).

17.4 Time Domain Representation of Free Energies in Terms of the Kernel $K(\cdot, \cdot)$

We now present the results on which the assertions of Sect. 17.2 are based.

Two equivalent versions of the argument will now be presented, one in the time domain, the other in the frequency domain. A formalism is developed in this section for the time domain and in Sect. 17.5 for the frequency domain, which extend the developments of Sect. 7.1.3 and allow us to apply the new strategy.

We treat (17.3.12)₁ as a first order partial differential equation for $G(s, u)$, $s, u \in \mathbb{R}^+$, where $K(s, u)$, $s, u \in \mathbb{R}^+$ is presumed to be known and has the property that

$$\int_0^\infty \int_0^\infty f(s)K(s, u)f(u)dsdu \leq 0 \tag{17.4.1}$$

for all choices of f such that the integral exists. We use the variables (7.1.29):

$$x = s + u, \quad y = s - u, \tag{17.4.2}$$

in terms of which (17.3.12)₁ becomes

$$\frac{\partial}{\partial x}G_n(x, y) = \frac{1}{2}K_n(x, y), \quad G_n(x, y) = G(s, u), \quad K_n(x, y) = K(s, u),$$

with general solution

$$G_n(x, y) = G_n(x_0, y) + \frac{1}{2} \int_{x_0}^x K_n(x', y)dx', \tag{17.4.3}$$

where x_0 is an arbitrary nonnegative real quantity. This is the scalar version of (7.1.30). It follows from (17.3.6)₁ and (17.3.14)₁ that

$$G_n(x, y) = G_n(x, -y) = G_n(x, |y|), \quad K_n(x, y) = K_n(x, -y) = K_n(x, |y|). \tag{17.4.4}$$

Observe that (17.3.9) yields

$$G(u) = G_n(u, u) = G_n(u, -u) = G_n(u, |u|), \quad u \in \mathbb{R}^+. \tag{17.4.5}$$

Putting

$$x' = s' + u', \quad y = s' - u' = s - u,$$

we have

$$s' = \frac{1}{2}(x' + y), \quad u' = \frac{1}{2}(x' - y).$$

In particular, these yield (s, u) corresponding to $x' = x$. Letting $x_0 \rightarrow \infty$ gives a solution of the form

$$G_n(x, y) = G_\infty - \frac{1}{2} \int_x^\infty K_n(x', y)dx'. \tag{17.4.6}$$

We have

$$\begin{aligned} G(s, u) &= G_n(x, y) = G_\infty - \frac{1}{2} \int_{s+u}^\infty K_n(x', s-u)dx' \\ &= G_\infty - \frac{1}{2} \int_{s+u}^\infty K\left(\frac{1}{2}(x' + s-u), \frac{1}{2}(x' - s+u)\right)dx'. \end{aligned}$$

Let us change the x' variable of integration to $z \geq 0$, defined by

$$x' = 2z + s + u, \tag{17.4.7}$$

so that

$$\tilde{G}(s, u) = - \int_0^\infty K(z + s, z + u) dz. \tag{17.4.8}$$

A similar relation for $\mathcal{G}(s, u)$ can be deduced from (17.3.5)₅ and (17.3.13).

We assume that $K(s, u)$ in (17.3.12)₁ is given, so that the rate of dissipation for a particular strain history of the material, specified by (17.3.11), is uniquely known. The following proposition will now be proved.

Proposition 17.4.1. *For free energy functionals and rates of dissipation of the forms (17.3.5) and (17.3.11), respectively, if we assume that the rate of dissipation is non-negative (which is the second law), then it follows that the integral term in (17.3.5)₄ is nonnegative.*

Thus, the property noted at the end of Remark 17.3.1 is confirmed.

Proof. Multiplying (17.4.8) by $\dot{E}^t(s)$ and $\dot{E}^t(u)$ and integrating yields

$$\begin{aligned} \psi(t) &= \phi(t) - \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s) \int_0^\infty K(z + s, z + u) dz \dot{E}^t(u) ds du \\ &= \phi(t) - \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) K(z + s, z + u) \dot{E}^t(u) ds du dz, \end{aligned} \tag{17.4.9}$$

on interchanging integrations. Now

$$\begin{aligned} \int_0^\infty \int_0^\infty \dot{E}^t(s) K(z + s, z + u) \dot{E}^t(u) ds du \\ = \int_z^\infty \int_z^\infty \dot{E}^t(v - z) K(v, w) \dot{E}^t(w - z) dv dw. \end{aligned}$$

Let us put

$$f(v) = \begin{cases} \dot{E}^t(v - z), & v \geq z \\ 0, & 0 \leq v < z \end{cases}$$

for arbitrary choices of \dot{E}^t . By virtue of assumption (17.4.1), it follows that the integral term in (17.4.9) is nonnegative. \square

We identify the relaxation function, in accordance with (17.3.9), as

$$G(s) = G(s, 0) = G_\infty - \int_0^\infty K(z + s, z) dz = G_\infty - \int_0^\infty K(z, z + s) dz, \tag{17.4.10}$$

which ensures that the condition P1 or (16.1.25) is satisfied. It follows from (17.4.10) that

$$\tilde{G}_0 = - \int_0^\infty K(z, z) dz, \tag{17.4.11}$$

using the notation of (16.1.4).

We take $s \geq u$ and $y = s - u$. Choosing $x_0 = y$ in (17.4.3), we have

$$\begin{aligned}
 G(s, u) &= G_n(s + u, s - u) = G(s - u) + \frac{1}{2} \int_{s-u}^{s+u} K_n(x', s - u) dx' \\
 &= G(s - u) + \int_{-u}^0 K(z + s, z + u) dz,
 \end{aligned} \tag{17.4.12}$$

where (17.4.5) and (17.4.7) have been used. Comparing the two solutions (17.4.8) and (17.4.12), we obtain

$$\begin{aligned}
 G(s - u) &= G_\infty - \int_{-u}^{\infty} K(z + s, z + u) dz \\
 &= G_\infty - \int_0^{\infty} K(w, w + s - u) dw,
 \end{aligned}$$

which agrees with (17.4.10). A similar result follows if we take $u \geq s$ and $y = u - s$. We can write (17.4.12) in a manner covering both cases as follows:

$$\begin{aligned}
 G(s, u) &= G(|s - u|) + \int_{-\min(s, u)}^0 K(z + s, z + u) dz \\
 &= G(|s - u|) + \int_0^{\min(s, u)} K(s - v, u - v) dv.
 \end{aligned}$$

This is the solution obeying the boundary conditions (17.3.9). Substituting this relation into the quadratic forms in (17.3.5)₄ and (17.3.19)₁, we obtain

$$\psi(t) = W(t) + \frac{1}{2} \int_0^\infty ds \int_0^\infty du \dot{E}^t(s) \int_0^{\min(s, u)} dv K(s - v, u - v) \dot{E}^t(u). \tag{17.4.13}$$

The integral term in (17.4.13) is non-positive by virtue of (17.3.21). It is of course the negative of the total dissipation $(-\mathcal{D}(t))$, by virtue of (16.1.29).

17.4.1 Some Examples

1. *Discrete-spectrum materials:* The kernels \tilde{G} and K have the form

$$\begin{aligned}
 \tilde{G}(s, u) &= \sum_{i, j=1}^n C_{ij} e^{-\alpha_i s - \alpha_j u}, \\
 K(s, u) &= - \sum_{i, j=1}^n (\alpha_i + \alpha_j) C_{ij} e^{-\alpha_i s - \alpha_j u},
 \end{aligned} \tag{17.4.14}$$

since if these are substituted into (17.3.5)₄ and (17.3.11)₁, they yield (16.3.13) and (16.3.15)_{2,3}. It is clear that (17.4.8) applied to (17.4.14)₂ yields (17.4.14)₁. Let the kernel $K(\cdot, \cdot)$ have the form

$$K(s, u) = - \sum_{i, j=1}^n \Gamma_{ij} e^{-\alpha_i s - \alpha_j u}, \tag{17.4.15}$$

where the symmetric matrix $\mathbf{\Gamma}$ with components Γ_{ij} , $i, j = 1, 2, \dots, n$ is nonnegative. The material is characterized by $\mathbf{\Gamma}$ and the vector $\boldsymbol{\alpha}$, with components α_i , $i = 1, 2, \dots, n$. These parameters are assumed to be known. Then, from (17.3.11)₁,

$$D(t) = \frac{1}{2} \sum_{i,j=1}^n \Gamma_{ij} e_i(t) e_j(t) = \frac{1}{2} \mathbf{e} \cdot \mathbf{\Gamma} \mathbf{e}, \tag{17.4.16}$$

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

This expression for $D(t)$ agrees with (16.3.15). The final relation is a definition of the vector quantity $\mathbf{e}(t)$, which is that introduced earlier by (16.3.12). Applying (17.4.8), we obtain

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

so that from (17.3.5)₂

$$\psi(t) = \phi(t) + \frac{1}{2} \sum_{i,j=1}^n \frac{\Gamma_{ij}}{\alpha_i + \alpha_j} e_i(t) e_j(t) = \phi(t) + \frac{1}{2} \mathbf{e} \cdot \mathbf{C} \mathbf{e}, \tag{17.4.17}$$

where the matrix \mathbf{C} has components of the form (see (16.3.15)₃)

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

The last form of (17.4.17) is of course (16.3.13). Then the relaxation function is given by

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

2. *The Dill free energy:* Using (17.3.5)₄, we put

$$K(s, u) = 2G'(s + u),$$

so that, from (17.4.8),

$$\tilde{G}(s, u) = \tilde{G}(s + u).$$

This yields the functional

$$\psi_{Dill}(t) = \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \tilde{G}(s_1 + s_2) \dot{E}^t(s_2) \dot{E}^t(s_1) ds_1 ds_2, \tag{17.4.18}$$

which is a free energy with rate of dissipation (*cf.* (17.3.11)₁) given by

$$D_{Dill}(t) = - \int_0^\infty \int_0^\infty G'(s_1 + s_2) \dot{E}^t(s_2) \dot{E}^t(s_1) ds_1 ds_2 \tag{17.4.19}$$

if and only if $G(\cdot)$ is completely monotonic, as defined in [89].
 For discrete-spectrum materials, these are given by

$$\psi_{Dill}(t) = \phi(t) + \frac{1}{2} \sum_{i=1}^n G_i e_i^2(t), \quad D_{Dill}(t) = \sum_{i=1}^n \alpha_i G_i e_i^2(t). \quad (17.4.20)$$

3. *Short-term memory free energy:* We now construct a new free energy. Let us consider $K(s, u)$ given by the product form $k(s)k(u)$ which guarantees non-negativity of the rate of dissipation. Consider

$$k(s) = ae^{-\lambda s^2}, \quad a, \lambda > 0, \quad (17.4.21)$$

which could be taken to model sharply declining or short-term memory behavior. Relation (17.4.21) yields

$$K(s, u) = -a^2 \exp[-\lambda(s^2 + u^2)] = -a^2 \exp\left[-\frac{1}{2}\lambda(x^2 + y^2)\right],$$

where the variables x and y are defined by (17.4.2). We obtain, from (17.4.6),

$$\begin{aligned} \tilde{G}(s, u) &= \frac{1}{2} \int_x^\infty a^2 \exp\left[-\frac{1}{2}\lambda((x')^2 + y^2)\right] dx' \\ &= \frac{1}{2} \sqrt{\frac{\pi}{2\lambda}} a^2 \left[1 - \Phi\left(\sqrt{\frac{\lambda}{2}}(s + u)\right)\right] \exp\left[-\frac{1}{2}\lambda(s - u)^2\right], \end{aligned} \quad (17.4.22)$$

where $\Phi(\cdot)$ is the probability integral [168]:

$$\Phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du.$$

From (17.4.10), (17.4.11), and (17.4.22), we have

$$\begin{aligned} \tilde{G}(s) &= \frac{1}{2} \sqrt{\frac{\pi}{2\lambda}} a^2 \left[1 - \Phi\left(\sqrt{\frac{\lambda}{2}}s\right)\right] \exp\left[-\frac{1}{2}\lambda s^2\right], \\ \tilde{G}_0 &= \frac{1}{2} \sqrt{\frac{\pi}{2\lambda}} a^2. \end{aligned}$$

17.5 Frequency Domain Representations of Free Energies in Terms of the Kernel $K_{+-}(\cdot, \cdot)$

The first discussion of the topic developed in this section was given in [158]. Also, special cases of the formulae given below, namely those relating to the minimum and associated free energies, were presented in [161] (see also (16.4.15)–(16.4.17)). One of our aims here is to provide generalizations of these formulae. However, our main

goal is to derive certain results which will prove more convenient for determining new free energy functionals.

Let us now consider free energies with general kernels. We define

$$Z_{+-}(\omega_1, \omega_2) = \int_0^\infty \int_0^\infty Z(s, u) e^{-i\omega_1 s + i\omega_2 u} ds du, \quad (17.5.1)$$

where $Z(s, u)$ represents any one of the kernels $\widetilde{G}(s, u)$, $K(s, u)$, or $Q(s, u)$. Note that

$$\overline{Z_{+-}}(\omega_1, \omega_2) = Z_{+-}(-\omega_1, -\omega_2) = Z_{+-}(\omega_2, \omega_1), \quad (17.5.2)$$

so that $Z_{+-}(\omega, \omega)$ is real. The quantity $Z_{+-}(\omega_1, \omega_2)$ is analytic in the lower half of the ω_1 complex plane and in the upper half of the ω_2 plane.

Note that

$$\begin{aligned} Z_{+-}(\omega_1, \omega_2) &= Z_{+-}(-\omega_2, -\omega_1), \\ \overline{Z_{+-}(\omega_1, \omega_2)} &= Z_{+-}(-\overline{\omega_1}, -\overline{\omega_2}) = Z_{+-}(\overline{\omega_2}, \overline{\omega_1}), \quad \omega_1, \omega_2 \in \Omega, \end{aligned} \quad (17.5.3)$$

where the property $Z(s, u) = Z(u, s)$ has been used. These relations hold if ω_1, ω_2 are points of analyticity of $Z_{+-}(\omega_1, \omega_2)$. It follows from (17.5.3) that $Z_{+-}(\omega_1, \omega_2)$ is real if $\overline{\omega_2} = \omega_1$. In particular, $Z_{+-}(\omega_0, \omega_0)$ is real if ω_0 is real. Thus, $Z_{+-}(\omega_1, \omega_2)$ is given by analytic continuation from the real axis for $\omega_1 \in \Omega^{(-)}$ and $\omega_2 \in \Omega^{(+)}$.

Inverting Fourier transforms in (17.5.1) yields that

$$Z(s, u) = \frac{1}{4\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty Z_{+-}(\omega_1, \omega_2) e^{i\omega_1 s - i\omega_2 u} d\omega_1 d\omega_2. \quad (17.5.4)$$

We shall not explicitly discuss the frequency domain version of the kernels $\mathcal{G}(s, u)$, $\mathcal{K}(s, u)$, and $\mathcal{Q}(s, u)$ in this section. These occur in quadratic forms expressed in terms of $E_{r+}^t(\omega)$ rather than $\dot{E}_+^t(\omega)$. We can, however, easily switch to this type of functional by using (16.1.17). Relations (17.3.12)₁, (17.3.23)₁, (17.3.24), and (17.5.1), yield that

$$\begin{aligned} i(\omega_1 - \omega_2)\widetilde{G}_{+-}(\omega_1, \omega_2) &= K_{+-}(\omega_1, \omega_2) + \widetilde{G}_+(\omega_1) + \overline{\widetilde{G}_+(\omega_2)} \\ &= K^{(1)}(\omega_1, \omega_2), \\ i(\omega_1 - \omega_2)Q_{+-}(\omega_1, \omega_2) &= -K_{+-}(\omega_1, \omega_2), \end{aligned} \quad (17.5.5)$$

where $\widetilde{G}_+(\omega)$ is defined by (16.1.7)₁. From (17.3.9), (16.1.7)₁, and (17.5.1), it follows that

$$\widetilde{G}_{+-}(\omega_1, \omega_2) \sim \begin{cases} \widetilde{G}_+(\omega_1) & \text{as } \omega_2 \rightarrow \infty, \\ \frac{-i\omega_2}{\overline{\widetilde{G}_+(\omega_2)}} & \\ \overline{\widetilde{G}_+(\omega_2)} & \text{as } \omega_1 \rightarrow \infty. \\ i\omega_1 \end{cases} \quad (17.5.6)$$

By an analogous argument to that yielding (17.5.6), we can deduce similar properties for $K_{+-}(\omega_1, \omega_2)$.

We can write (17.3.5)₄, (17.3.11)₁, and (17.3.16)₁ in the forms

$$\begin{aligned} \psi(t) &= \phi(t) + \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} \widetilde{G}_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2, \\ D(t) &= -\frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2, \\ \mathcal{D}(t) &= \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} \underline{Q}_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2, \end{aligned} \tag{17.5.7}$$

where $\dot{E}_+^t(\omega)$ is defined by (16.1.17). Note that (17.5.7)₂ can be written in the form

$$D(t) = -\frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{E_{r+}^t(\omega_1)} \omega_1 \omega_2 K_{+-}(\omega_1, \omega_2) E_{r+}^t(\omega_2) d\omega_1 d\omega_2,$$

by virtue of (16.1.17). A similar observation applies to (17.5.7)_{1,3}. Using the analyticity properties of the kernels (see (16.1.24)), we can write (17.5.7) in the form

$$\begin{aligned} \psi(t) &= \phi(t) + \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_F^t(\omega_1)} \widetilde{G}_{+-}(\omega_1, \omega_2) \dot{E}_F^t(\omega_2) d\omega_1 d\omega_2, \\ D(t) &= -\frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_F^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_F^t(\omega_2) d\omega_1 d\omega_2, \\ \mathcal{D}(t) &= \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_F^t(\omega_1)} \underline{Q}_{+-}(\omega_1, \omega_2) \dot{E}_F^t(\omega_2) d\omega_1 d\omega_2, \end{aligned} \tag{17.5.8}$$

where $E_F^t(\omega)$ is defined by (16.1.24)₂. Referring to Remark 17.3.3, we see that (17.5.8) corresponds to case (b) of (17.3.18), as is also true for (16.1.24).

As for the time domain expressions, we conclude from P2 and P3 (see (16.1.26), (16.1.28)) that the quadratic functionals in (17.5.7)₁ and (17.5.7)₃ must be nonnegative, while those in (17.5.7)₂ must be nonpositive. A similar statement applies to (17.5.8). We seek therefore to write down the analogue of (17.3.15). It follows from (17.5.8) that

$$\widetilde{G}_{+-}(\omega, \omega) \geq 0, \quad K_{+-}(\omega, \omega) \leq 0 \quad \forall \omega \in \mathbb{R}. \tag{17.5.9}$$

Relations (17.5.9) do not follow from (17.5.7) because of the analyticity properties of $\dot{E}_+^t(\omega)$ which, as we will see in Sect. 17.5.2, allow considerable non-uniqueness in the kernels of (17.5.7), so that in particular the diagonal quantities ($\omega_1 = \omega_2$) are not unique. Such non-uniqueness is not present in (17.5.8). The quantity $\underline{Q}_{+-}(\omega_1, \omega_2)$ is excluded because it contains singularities at $\omega_1 = \omega_2$, which arises from the fact that (17.3.19)_{3,4} can be written in the form (17.5.8) but with a delta function.

It follows from (17.5.5)₂ that

$$\psi(t) = \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K^{(1)}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2. \tag{17.5.10}$$

The notation in the denominator of this last form means that if we integrate first over ω_1 , it becomes $(\omega_1 - \omega_2^-)$ or if ω_2 first then it is $(\omega_1^+ - \omega_2)$. This choice of denominator, rather than $(\omega_1^- - \omega_2^+)$, is initially assigned by using the example given by (16.4.15). It will be justified below by means of a general argument. The terms in $K^{(1)}$ depending

only on one variable (ω_1 or ω_2) do not contribute to the integral. To see this, consider, for example, the term

$$-\frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} \widetilde{G}_+(\omega_1) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 \tag{17.5.11}$$

and carry out the integral over ω_2 , completing the contour over $\Omega^{(-)}$, on which $\dot{E}_+^t(\omega_2)$ is analytic. The denominator becomes $\omega_1^+ - \omega_2$. The infinite part of the contour yields a vanishing contribution, by virtue of (16.1.20), so the result is zero. We note, however, for later use that if ω_1^+ were replaced by ω_1^- , the result would be

$$-\frac{1}{4\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} \widetilde{G}_+(\omega_1) \dot{E}_+^t(\omega_1) d\omega_1. \tag{17.5.12}$$

Thus, (17.5.10) can be replaced by

$$\begin{aligned} \psi(t) &= \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 \\ &= \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{E_{r+}^t(\omega_1)} \omega_1 \omega_2 K_{+-}(\omega_1, \omega_2) E_{r+}^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2, \end{aligned} \tag{17.5.13}$$

on using (16.1.17). Let us apply the Plemelj formulae to the integral in (17.5.13)₁ over ω_1 to obtain

$$\begin{aligned} \psi(t) &= \phi(t) - \frac{i}{8\pi^2} P \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2 \\ &\quad - \frac{1}{8\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega)} K_{+-}(\omega, \omega) \dot{E}_+^t(\omega) d\omega, \end{aligned} \tag{17.5.14}$$

where the symbol “ P ” indicates a principal value integral over ω_1 . Also, consider the integral (see (17.5.5)₃)

$$\mathcal{D}_1(t) = \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2.$$

Differentiating with respect to t , we find, with the aid of (16.1.18)₁, that

$$\dot{\mathcal{D}}_1(t) = D(t), \tag{17.5.15}$$

where $D(t)$ is given by (17.5.7)₂. The relation

$$\int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2)}{\omega_1^- - \omega_2} d\omega_2 = 0, \tag{17.5.16}$$

and a similar one involving integration over ω_1 , have been used. Equation (17.5.16) follows by closing the contour on $\Omega^{(+)}$ and recalling that a property similar to (17.5.6)

applies to $K_{+-}(\omega_1, \omega_2)$. Relation (17.5.15) implies that $\mathcal{D}_1(t) = \mathcal{D}(t) + k$, where k is a constant which can be shown to be zero because $\mathcal{D}_1(-\infty) = 0 = \mathcal{D}(-\infty)$. This follows by observing that \dot{E}_+^t , given by (16.1.17), tends to zero as $t \rightarrow -\infty$, because of assumption (16.1.2). We conclude that

$$\begin{aligned} \mathcal{D}(t) = \mathcal{D}_1(t) &= \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2 \\ &= \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{E_{r+}^t(\omega_1)} \omega_1 \omega_2 K_{+-}(\omega_1, \omega_2) E_{r+}^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2. \end{aligned} \quad (17.5.17)$$

In a similar manner to the derivation of (17.5.14), we have

$$\begin{aligned} \mathcal{D}(t) &= \frac{i}{8\pi^2} P \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2 \\ &\quad - \frac{1}{8\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega)} K_{+-}(\omega, \omega) \dot{E}_+^t(\omega) d\omega. \end{aligned}$$

Therefore,

$$\begin{aligned} \psi(t) + \mathcal{D}(t) &= \phi(t) - \frac{1}{4\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega)} K_{+-}(\omega, \omega) \dot{E}_+^t(\omega) d\omega \\ &= \phi(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega)} \frac{H(\omega)}{\omega^2} \dot{E}_+^t(\omega) d\omega, \end{aligned}$$

by virtue of (16.1.29) and (17.3.19) for arbitrary histories. It follows from this result together with (16.1.7)₁ and (16.1.13) that

$$\begin{aligned} K_{+-}(\omega, \omega) &= -2 \frac{H(\omega)}{\omega^2} = -2\widetilde{G}_c(\omega) \\ &= -\frac{G'_+(\omega)}{i\omega} + \frac{\overline{G'_+(\omega)}}{i\omega} = -\widetilde{G}_+(\omega) - \overline{\widetilde{G}_+(\omega)}, \end{aligned} \quad (17.5.18)$$

where (16.1.8) has also been invoked. This relation can in fact be shown directly. From (17.5.1), we can write

$$K_{+-}(\omega, \omega) = \int_0^{\infty} \int_0^{\infty} K(s, u) e^{-i\omega(s-u)} ds du.$$

Transforming to the variables x, y defined by (17.4.2), we obtain

$$\begin{aligned} K_{+-}(\omega, \omega) &= -\frac{1}{2} \int_0^{\infty} dx \int_{-x}^x dy K_n(x, y) e^{-i\omega y} \\ &= -\int_0^{\infty} dx \int_0^x dy K_n(x, y) \cos \omega y, \end{aligned}$$

where (17.4.4) has been used. We can write this in the form

$$\begin{aligned} K_{+-}(\omega, \omega) &= - \int_0^\infty dy \int_y^\infty dx K_R(x, y) \cos \omega y \\ &= -2 \int_0^\infty \tilde{G}(y) \cos \omega y dy = -2\tilde{G}_c(\omega), \end{aligned}$$

by virtue of (17.4.6) and (17.4.5). This proves the result.

Remark 17.5.1. We see from this derivation that the constraint in the time domain equivalent to (17.5.18) is (17.4.5) combined with (17.4.6) (which yield (17.4.10)). Relation (17.4.5) (or (17.3.9)) is of course the property P1 or (16.1.25). The frequency domain form (17.5.18) is more useful for deriving explicit forms of free energies, as we shall see.

Remark 17.5.2. Relation (17.5.18) can be used to prove P1 or (16.1.25), from (17.5.13)₂, by differentiating the latter equation with respect to $E(t)$.

Note that (17.5.18) implies that $K^{(1)}(\omega, \omega)$, defined by (17.5.5)₂, vanishes. The quantity $K_{+-}(\omega, \omega)$ is independent of the choice of free energy. Observe that (17.5.18) is consistent with (17.5.9)₂. Both the non-positivity of $K_{+-}(\omega, \omega)$ and the non-negativity of $H(\omega)$ are direct consequences of the second law (see P3 after (16.1.28), (16.1.12) and (16.1.13)).

If we were to take the other choice of denominator, namely $\omega_1^- - \omega_2^+$, in (17.5.13) and $\omega_1^+ - \omega_2^-$ in (17.5.17), there would be a positive sign on $2H(\omega)/\omega^2$ in (17.5.18)₁, which contradicts the second law, as expressed by (17.5.9)₂.

We now show that (17.4.9) is the time domain version of (17.5.13)₁. Substituting (17.5.4) for $Z(s, u) = K(s, u)$ into (17.4.8)₁ yields

$$\begin{aligned} \tilde{G}(s, u) &= -\frac{1}{4\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \int_0^\infty K_{+-}(\omega_1, \omega_2) e^{i\omega_1(s+z) - i\omega_2(u+z)} dz d\omega_1 d\omega_2 \\ &= -\frac{i}{4\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{K_{+-}(\omega_1, \omega_2)}{\omega_1^+ - \omega_2^-} e^{i\omega_1 s - i\omega_2 u} d\omega_1 d\omega_2. \end{aligned} \tag{17.5.19}$$

The denominator results from putting

$$e^{i(\omega_1 - \omega_2)z} = e^{i(\omega_1 - \omega_2^-)z} = e^{i(\omega_1^+ - \omega_2)z}, \tag{17.5.20}$$

which ensures that the integral over z exists. If $\tilde{G}(s, u)$, given by (17.5.19), is inserted into (17.3.5)₄, we obtain (17.5.13)₁. The argument based on (17.5.20) is perhaps the simplest way of showing that the denominator in (17.5.13) is the correct choice, rather than the alternative in (17.5.17).

Using (16.1.25) to obtain the form of the stress function from (17.5.13)₁, we find, by virtue of (16.1.17), that

$$T(t) = T_e(t) - \frac{i}{4\pi^2} \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{K_{+-}(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2.$$

This involves combining two terms which can be shown to be equal with the help of (17.5.2). Carrying out the ω_1 integration by closing the contour on $\Omega^{(-)}$ and using (17.5.18), we obtain (16.1.23)₂.

Thus, if $K_{+-}(\omega_1, \omega_2)$ is given for all ω_1 and $\omega_2 \in \mathbb{R}$, the material is completely characterized by (17.5.13) and (17.5.18).

Relations (16.4.15) and (16.4.17) are special cases of (17.5.13)₂ and (17.5.7)₂ (the latter expressed in terms of E_{r+}^t), where

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

while (16.4.16) is a special case of (17.5.17)₂. Also, replacements corresponding to (17.5.22) below can be implemented here. The particular case referred to in Remark 17.5.3 is obtained by subtracting a term $H_+^f(\omega_2)H_-^f(\omega_1)$ from the kernels in (16.4.15), which yields an alternative expression involving non-singular integrals:

$$\begin{aligned} \psi_f(t) &= \phi(t) + \frac{i}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{E_{r+}^t(\omega_1)}N(\omega_1, \omega_2)E_{r+}^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2, \\ N(\omega_1, \omega_2) &= H_+^f(\omega_1)H_-^f(\omega_2) - H_+^f(\omega_2)H_-^f(\omega_1). \end{aligned}$$

This is a special case of (17.5.26) below, with $\dot{E}_+^t(\omega)$ replaced by $-i\omega E_{r+}^t(\omega)$, by virtue of (16.1.17). Using the same relation, we can interchangeably express the above formulae in terms of $\dot{E}_+^t(\omega)$ or $E_{r+}^t(\omega)$.

17.5.1 Example: Discrete-Spectrum Materials

This was already discussed in the context of the time domain theory, as expressed by (17.4.14). From (17.5.1) and (17.4.15), it follows that

$$\begin{aligned} K_{+-}(\omega_1, \omega_2) &= - \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + i\omega_1)(\alpha_j - i\omega_2)}, \\ \tilde{G}_{+-}(\omega_1, \omega_2) &= \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)(\alpha_i + i\omega_1)(\alpha_j - i\omega_2)}, \\ \tilde{G}_+(\omega) &= \sum_{i=1}^n \frac{G_i}{\alpha_i + i\omega} = \sum_{i,j=1}^n \frac{\Gamma_{ij}}{(\alpha_i + \alpha_j)(\alpha_i + i\omega)}. \end{aligned} \tag{17.5.21}$$

The formula for $\tilde{G}_+(\omega)$ also follows from (17.5.6). Observe that

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

by virtue of (17.5.21)_{3,4}. This agrees with (17.5.18).

The positivity of the individual G_j is not in itself a requirement. What is important is that $\widetilde{G}_c(\omega)$ be nonnegative, as required by (16.1.12). Now, from (17.5.21)₄,

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

This is the sum of two terms, one proportional to ω^2 in the numerator, and the other proportional to $\alpha_i \alpha_j$. Both of these can be seen to be separately nonnegative, on recalling that Γ is a nonnegative matrix, so we have the desired property (16.1.12).

17.5.2 Non-uniqueness of the Kernels

We now consider how the kernels in (17.5.7) are not unique. This phenomenon is the frequency domain version of Causality constraints outlined in Remark 17.3.3. We deal here with case (a) of (17.3.18). Using the same argument as that leading to (16.1.22), we can express (17.5.7) in different forms. Consider the replacement

$$Z_{+-}(\omega_1, \omega_2) \rightarrow Y(\omega_1, \omega_2) = Z_{+-}(\omega_1, \omega_2) + z_{2+}(\omega_1, \omega_2) + z_{1-}(\omega_1, \omega_2), \quad (17.5.22)$$

where $Z_{+-}(\omega_1, \omega_2)$ becoming $Y(\omega_1, \omega_2)$ represents either $K_{+-}(\omega_1, \omega_2)$ becoming $L(\omega_1, \omega_2)$ or $\widetilde{G}_{+-}(\omega_1, \omega_2)$ becoming $R(\omega_1, \omega_2)$, both of which will be used later. The functions $z_{2+}(\omega_1, \omega_2)$ and $z_{1-}(\omega_1, \omega_2)$ correspondingly represent $k_{2+}(\omega_1, \omega_2)$ and $k_{1-}(\omega_1, \omega_2)$ for $K_{+-}(\omega_1, \omega_2)$ and $g_{2+}(\omega_1, \omega_2)$ and $g_{1-}(\omega_1, \omega_2)$ for $\widetilde{G}_{+-}(\omega_1, \omega_2)$, respectively.

The function $z_{2+}(\omega_1, \omega_2)$ has singularities on the ω_2 complex plane only in $\mathcal{Q}^{(+)}$ and $z_{1-}(\omega_1, \omega_2)$ has singularities on the ω_1 complex plane only in $\mathcal{Q}^{(-)}$.

Such substitutions leave the relations in (17.5.7) unchanged, as may be seen by closing the relevant integral on $\mathcal{Q}^{(\pm)}$ as appropriate, and invoking Cauchy's theorem. It is required, however, that the contributions from the infinite parts of the contours vanish. Noting (16.1.20) in this context, we see that the quantities $k_{2+}(\omega_1, \omega_2)$, $k_{1-}(\omega_1, \omega_2)$ and $g_{2+}(\omega_1, \omega_2)$, $g_{1-}(\omega_1, \omega_2)$ must decay to zero at large ω_1 or ω_2 .

Similar substitutions can be made for Q_{+-} in (17.5.7)₃.

Interesting special cases are as follows:

$$\begin{aligned} Y(\omega_1, \omega_2) &= Z_{+-}(\omega_1, \omega_2) + a_1 Z_{+-}(-\omega_1, \omega_2) + a_2 Z_{+-}(\omega_1, -\omega_2) \\ &\quad + a_3 Z_{+-}(-\omega_1, -\omega_2), \end{aligned}$$

where the a_i , $i = 1, 2, 3$, are arbitrary complex constants which may be different for each quantity represented by Z . Similar remarks apply to $Q_{+-}(\omega_1, \omega_2)$.

Remark 17.5.3. If we choose $a_1 = a_2 = 0$ and $a_3 = -1$, then from (17.5.2), it follows that $Y(\omega, \omega) = 0$.

Thus, we can write a general form of (17.5.7)_{1,2}, incorporating substitutions of the kind outlined above, as follows:

$$\begin{aligned} \psi(t) &= \phi(t) + \frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} R(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2 \\ D(t) &= -\frac{1}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega_1)} L(\omega_1, \omega_2) \dot{E}_+^t(\omega_2) d\omega_1 d\omega_2, \end{aligned} \tag{17.5.23}$$

in the notation specified after (17.5.22), so that, for example,

$$L(\omega_1, \omega_2) = K_{+-}(\omega_1, \omega_2) + k_{2+}(\omega_1, \omega_2) + k_{1-}(\omega_1, \omega_2).$$

If (17.5.7) is replaced by (17.5.8), the non-uniqueness of the kernels no longer holds, as noted after (17.5.9). Equation (17.5.23)₁ can be replaced by

$$\psi(t) = \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} L(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2, \tag{17.5.24}$$

by virtue of the relation

$$-\frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} [k_{2+}(\omega_1, \omega_2) + k_{1-}(\omega_1, \omega_2)] \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2 = 0,$$

so that (17.5.24) reduces to (17.5.13)₁. The term $k_{2+}(\omega_1, \omega_2)$ yields zero by integrating the variable ω_2 over a contour enclosing $\mathcal{Q}^{(-)}$, which is a generalization of the argument relating to (17.5.11). Similarly for the term $k_{1-}(\omega_1, \omega_2)$, which is zero by virtue of the integration over ω_1 .

However, for $\mathcal{D}(t)$, we have

$$\begin{aligned} \mathcal{D}(t) &= \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} L(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^- - \omega_2^+} d\omega_1 d\omega_2 \\ &\quad + \frac{1}{4\pi} \int_{-\infty}^{\infty} \overline{\dot{E}_+^t(\omega)} [k_{2+}(\omega, \omega) + k_{1-}(\omega, \omega)] \dot{E}_+^t(\omega) d\omega. \end{aligned} \tag{17.5.25}$$

This follows by a generalization of the argument leading to (17.5.12). Applying the Plemelj formulae to (17.5.24) and (17.5.25), we find that the condition (17.5.18) re-emerges.

Note that if

$$L(\omega_1, \omega_2) = K_{+-}(\omega_1, \omega_2) - K_{+-}(-\omega_1, -\omega_2),$$

as specified by Remark 17.5.3, then the integrals in (17.5.24) and (17.5.25) are non-singular because $L(\omega, \omega)$ vanishes, by virtue of (17.5.2). Thus,

$$\psi(t) = \phi(t) - \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} L(\omega_1, \omega_2) \dot{E}_+^t(\omega_2)}{\omega_1 - \omega_2} d\omega_1 d\omega_2. \tag{17.5.26}$$

The general forms of free energies or dissipation functionals can be specialized in two ways: specifying histories or choosing particular functional forms for the rate of dissipation kernels $K(\cdot, \cdot)$. We now explore both of these approaches.

17.6 General Dissipative Materials for Specified Histories

In this section, we choose general kernels and particular histories.

As noted in Sect. 17.2, a given material with memory typically has a set of many free energy functionals associated with it, all members of which yield the same constitutive relations. Explicit formulae are derived in this chapter for the free energy and total dissipation of such a material in the cases of step function and sinusoidal/exponential histories. Expressions for the fraction of stored and dissipated energy are deduced.

17.6.1 Free Energy and Dissipation Functionals for Particular Histories

Two important dimensionless parameters are

$$\beta = \frac{G_\infty}{G_0}, \quad \chi = \frac{G_0 - G_\infty}{G_0} = 1 - \beta = -\frac{1}{G_0} \int_0^\infty K(z, z) dz, \quad \beta, \chi \in [0, 1]. \quad (17.6.1)$$

The relation (17.3.15) has been used. These parameters provide simple measures of the memory contribution and therefore, the amount of energy loss due to material deformation. The smaller the quantity β or the larger the parameter χ , the greater the energy loss.

The fraction of energy stored and dissipated, respectively, for any given history, can be determined according to the formulae

$$F_s(t) = \frac{\psi(t)}{W(t)}, \quad F_d(t) = \frac{\mathcal{D}(t)}{W(t)}, \quad F_s(t) + F_d(t) = 1. \quad (17.6.2)$$

The interpretation of these quantities is discussed further in [18].

Expressions for the free energy, total dissipation, and the ratios $F_s(t)$, $F_d(t)$ will be given in the case of a general rate of dissipation kernel $K(s, u)$, and three different types of strain history. These quantities are important characteristic properties of the material described by this kernel.

Any choice of $K(s, u) \in \mathcal{K}$ will describe the stress-strain and energy behavior of one specific material. Matters are more difficult when we seek to reverse this process and determine the kernel $K(s, u)$ which describe a pre-chosen material, referred to as material I in Sect. 17.1.

Let the quantity $K_{+-}(\omega_1, \omega_2)$, determined from each $K(s, u) \in \mathcal{K}$ by (17.5.1), form a set \mathcal{K}_F .

As already noted, the functionals $\psi_f(t)$, $f = 1, 2, \dots, N$ lie on the boundary of \mathcal{F} , in particular the minimum and maximum free energies which provide lower and upper bounds; similarly for $K_{+-}^f(\omega_1, \omega_2)$ with respect to \mathcal{K}_F . The factors $H_\pm^f(\omega)$ and therefore all these quantities are deduced from the parameters of the relaxation function. The size of the set \mathcal{F} (and \mathcal{K}_F or \mathcal{K}) is, in this sense, determined by the relaxation function.

We seek to give detailed expressions for free energies and related quantities for general choices of the kernel $K(s, u) \in \mathcal{K}$ and histories with step function and SE behavior.

17.6.1.1 Step Function Histories

This is the simplest non-constant behavior of the strain history, given as follows. Consider $E(u)$, $u \leq t$ where t is the current time, assumed to be positive. Let

$$E(u) = \begin{cases} 0, & u \leq 0, \\ E_0, & 0 < u \leq t, \end{cases} \tag{17.6.3}$$

giving

$$\dot{E}(u) = \frac{dE(u)}{du} = E_0\delta(u),$$

in terms of the singular delta function. Thus,

$$\dot{E}^t(s) = E_0\delta(t - s).$$

It follows from this relation and (17.3.11) that

$$D(t) = -\frac{E_0^2}{2}K(t, t). \tag{17.6.4}$$

Also, from (17.4.8), (17.3.5)₄ and (16.1.32), we have

$$\begin{aligned} \psi(t) &= \phi(t) - \frac{E_0^2}{2} \int_0^\infty K(t + z, t + z) dz \\ &= \frac{1}{2}G_\infty E_0^2 - \frac{E_0^2}{2} \int_t^\infty K(y, y) dy, \quad t \geq 0. \end{aligned} \tag{17.6.5}$$

The integral term is nonnegative, by virtue of (17.3.15). Relation (17.4.11) yields that

$$\frac{1}{2}G_0 E_0^2 = \frac{1}{2}G_\infty E_0^2 - \frac{E_0^2}{2} \int_0^\infty K(y, y) dy. \tag{17.6.6}$$

Thus,

$$\psi(t) \leq \frac{1}{2}G_0 E_0^2.$$

It follows from (17.3.19) that

$$W(t) = \frac{1}{2}G_0 E_0^2,$$

so that (17.3.21) is satisfied. Relation (16.1.29) gives that

$$\mathcal{D}(t) = -\frac{E_0^2}{2} \int_0^t K(y, y) dy.$$

The finite range of the integral is easily understood, from a physical point of view. For the infinite period specified by (17.6.3)₁, there is no dissipation. At time $t = 0$, dissipation begins. Referring to (17.6.2), we see that

$$F_d(t) = -\frac{1}{G_0} \int_0^t K(y, y) dy, \quad F_s(t) = 1 - F_d(t).$$

Differentiating with respect to time, we obtain

$$\frac{d}{dt} F_d(t) = -\frac{1}{G_0} K(t, t), \quad \frac{d}{dt} F_s(t) = -\frac{d}{dt} F_d(t),$$

so that $F_d(t)$ is monotonically increasing and $F_s(t)$ is monotonically decreasing. Note that

$$F_d(\infty) = \frac{G_0 - G_\infty}{G_0} = \chi = 1 - \beta, \quad F_s(\infty) = \frac{G_\infty}{G_0} = \beta,$$

in terms of the quantities introduced in (17.6.1). Thus, χ measures the energy dissipation and β the energy storage for any material in \mathcal{K} , due to a sudden step change in strain.

The quantity $F_d(t)$ is zero at $t = 0$ and increases monotonically to χ as $t \rightarrow \infty$, while $F_s(t) = 1$ at $t = 0$ and decreases monotonically to β at large t . Note that $K(y, y)$ must tend to zero as $y \rightarrow \infty$ to yield convergent integrals in (17.6.5) or (17.6.6).

Observe from (17.6.4) that, if $D(t)$ can be determined, this yields a measurement of $K(t, t)$. To obtain measurements of $K(s, u)$, $s, u \in R^+$, one needs to consider histories with two steps (Sect. 7.1.3). Of course, this is not a very practical technique since step function histories are difficult to approximate closely.

17.6.1.2 SSE Histories

Consider the history and current value $(E^t, E(t))$ defined by (16.11.1). Furthermore, ω_\pm are given by (16.11.2). For $\eta = 0$, we have purely sinusoidal behavior, while for $\omega_0 = 0$, the history is exponentially growing. The derivative $\dot{E}^t(s)$ has the form

$$\dot{E}^t(s) = i\omega_- E_0 e^{i\omega_-(t-s)} - i\omega_+ \overline{E_0} e^{-i\omega_+(t-s)}. \quad (17.6.7)$$

Also, the quantity $E_+^t(\omega)$ is given by

$$E_+^t(\omega) = E_0 \frac{e^{i\omega_- t}}{i(\omega + \omega_-)} + \overline{E_0} \frac{e^{-i\omega_+ t}}{i(\omega - \omega_+)}, \quad (17.6.8)$$

while

$$\dot{E}_+^t(\omega) = E_0 \omega_- \frac{e^{i\omega_- t}}{\omega + \omega_-} - \overline{E_0} \omega_+ \frac{e^{-i\omega_+ t}}{\omega - \omega_+} = -i\omega E_{r+}^t(\omega), \quad (17.6.9)$$

by virtue of (16.1.17).

Using (16.1.3) and (17.6.7), we find that the stress is given by

$$T(t) = \mathcal{M}_+(\omega_-) E_0 e^{i\omega_- t} + \mathcal{M}_+(-\omega_+) \overline{E_0} e^{-i\omega_+ t}, \quad (17.6.10)$$

where $\mathcal{M}_+(\omega)$ is defined by (16.1.9). Referring to (17.6.8) and (17.6.9), we see that

$$E_+^t(-i\alpha) = E_0 \frac{e^{i\omega_- t}}{\alpha + i\omega_-} + \overline{E_0} \frac{e^{-i\omega_+ t}}{\alpha - i\omega_+},$$

$$\dot{E}_+^t(-i\alpha) = iE_0 \frac{\omega_- e^{i\omega_- t}}{\alpha + i\omega_-} - i\overline{E_0} \frac{\omega_+ e^{-i\omega_+ t}}{\alpha - i\omega_+}.$$

It follows from (17.6.9) that

$$E_{r+}^t(-i\alpha_i) = -iE_0 \frac{\omega_-}{\alpha_i} \frac{e^{i\omega_- t}}{\alpha_i + i\omega_-} + i\overline{E_0} \frac{\omega_+}{\alpha_i} \frac{e^{-i\omega_+ t}}{\alpha_i - i\omega_+}$$

$$= -\frac{e_i(t)}{\alpha_i}, \quad i = 1, 2, \dots, n,$$

where the e_i are given by (17.4.16) with the aid of (16.1.17).

The real quadratic form

$$V(t) = ME_0^2 e^{2i\omega_- t} + \overline{M} \overline{E_0}^2 e^{-2i\omega_+ t} + N|E_0|^2 e^{i(\omega_- - \omega_+)t}$$

$$= 2\operatorname{Re}[ME_0^2 e^{2i\omega_- t}] + N|E_0|^2 e^{i(\omega_- - \omega_+)t} \quad (17.6.11)$$

$$= \left[2\operatorname{Re}\left(ME_0^2 e^{2i\omega_0 t} \right) + N|E_0|^2 \right] e^{2\eta t}$$

will be denoted by

$$V(t) = \{M, N\}. \quad (17.6.12)$$

which is a generalization of (16.11.3). The quantity N is real. All free energies, total dissipations, rates of dissipation and work functions can be represented in the form $V(t)$, for histories given by (16.11.1). Note that

$$\int_{-\infty}^t V(s) ds = \left\{ \frac{M}{2i\omega_-}, \frac{N}{i(\omega_- - \omega_+)} \right\}, \quad (17.6.13)$$

$$\dot{V}(t) = \{2i\omega_- M, i(\omega_- - \omega_+)N\}.$$

Remark 17.6.1. For $\eta = 0$, the quantity $V = \{M, N\}$ will be completely periodic if M and N are finite quantities, independent of t .

We have, from (17.6.7) for $s = 0$ and (17.6.10),

$$T(t)\dot{E}(t) = i\omega_- \mathcal{M}_+(\omega_-) E_0^2 e^{2i\omega_- t} - i\omega_+ \mathcal{M}_+(-\omega_+) \overline{E_0}^2 e^{-2i\omega_+ t}$$

$$+ i[\omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)] |E_0|^2 e^{i(\omega_- - \omega_+)t} \quad (17.6.14)$$

$$= \{i\omega_- \mathcal{M}_+(\omega_-), i[\omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)]\}.$$

Using (16.1.30)₁, (17.6.13)₁, and (17.6.14), we see that

$$W(t) = \{M_W, N_W\},$$

where

$$M_W = \frac{1}{2}\mathcal{M}_+(\omega_-), \quad N_W = \frac{\omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)}{\omega_- - \omega_+}. \quad (17.6.15)$$

The term N_W diverges in the purely sinusoidal limit as $\eta \rightarrow 0$.

A general free energy (17.3.5)₁ for histories of the form (16.11.1) is given by

$$\psi(t) = \{M_\psi, N_\psi\}. \quad (17.6.16)$$

where

$$\begin{aligned} M_\psi &= \frac{1}{2} \left[G_\infty - \omega_-^2 \widetilde{G}_{+-}(\omega_-, -\omega_-) \right] \\ &= \frac{1}{2} \left[\mathcal{M}_+(\omega_-) + \frac{i\omega_-}{2} K_{+-}(\omega_-, -\omega_-) \right], \end{aligned} \quad (17.6.17)$$

by virtue of (16.1.9), (17.5.1), and (17.5.5). Also, from (16.1.9), (17.5.3)₁ and subsequent observations,

$$\begin{aligned} N_\psi &= G_\infty + \frac{1}{2} \left\{ |\omega_-|^2 \widetilde{G}_{+-}(\omega_-, \omega_+) + |\omega_+|^2 \widetilde{G}_{+-}(-\omega_+, -\omega_-) \right\} \\ &= G_\infty + |\omega_-|^2 \widetilde{G}_{+-}(\omega_-, \omega_+) \\ &= G_\infty + \frac{|\omega_-|^2}{i(\omega_- - \omega_+)} \left[K_{+-}(\omega_-, \omega_+) + \widetilde{G}_+(\omega_-) + \overline{\widetilde{G}_+}(\omega_+) \right] \\ &= \frac{-i|\omega_-|^2 K_{+-}(\omega_-, \omega_+) + \omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)}{\omega_- - \omega_+}, \end{aligned} \quad (17.6.18)$$

again using (17.5.5). From (17.3.11), (17.5.3), and (17.6.7), we find that

$$D(t) = \{M_D, N_D\}, \quad (17.6.19)$$

where

$$\begin{aligned} M_D &= \frac{\omega_-^2}{2} K_{+-}(\omega_-, -\omega_-), \\ N_D &= -\frac{|\omega_-|^2}{2} \{K_{+-}(\omega_-, \omega_+) + K_{+-}(-\omega_+, -\omega_-)\} \\ &= -|\omega_-|^2 K_{+-}(\omega_-, \omega_+). \end{aligned} \quad (17.6.20)$$

Let

$$\mathcal{D}(t) = \{M_{\mathcal{D}}, N_{\mathcal{D}}\}.$$

Then, from (17.6.13)₁,

$$M_{\mathcal{D}} = -\frac{i\omega_-}{4} K_{+-}(\omega_-, -\omega_-), \quad N_{\mathcal{D}} = i|\omega_-|^2 \frac{K_{+-}(\omega_-, \omega_+)}{\omega_- - \omega_+}. \quad (17.6.21)$$

We see from (17.6.15), (17.6.17), (17.6.18), and (17.6.21) that (16.1.29) is obeyed. Note that $N_{\mathcal{D}}$ diverges in the sinusoidal limit.

The ratios (17.6.2) are given by

$$F_d(t) = \frac{V_{\mathcal{D}}(t)}{V_W(t)}, \quad F_s(t) = 1 - F_d(t),$$

where $V_{\mathcal{D}}(t)$ has the form (17.6.11) with $M = M_{\mathcal{D}}$ and $N = N_{\mathcal{D}}$ given by (17.6.21). Also, $V_W(t)$ is similarly defined, with M_W and N_W given by (17.6.15).

The factor $e^{2\eta t}$, giving the exponential part of the history, cancels out of the ratios, yielding for $F_d(t)$,

$$F_d(t) = \frac{M_{\mathcal{D}}E_0^2 e^{2i\omega_0 t} + \overline{M_{\mathcal{D}}E_0^2} e^{-2i\omega_0 t} + N_{\mathcal{D}}|E_0|^2}{M_W E_0^2 e^{2i\omega_0 t} + \overline{M_W E_0^2} e^{-2i\omega_0 t} + N_W |E_0|^2}. \quad (17.6.22)$$

Now, we have

$$M_W E_0^2 e^{2i\omega_0 t} + \overline{M_W E_0^2} e^{-2i\omega_0 t} + N_W |E_0|^2 > 0, \quad (17.6.23)$$

which is a consequence of the fact that $W(t)$, given by (17.3.19), is positive, as is the cancelled factor $e^{2\eta t}$. Also, by averaging over any interval of duration π/ω_0 , the oscillatory terms vanish and we deduce that $N_W > 0$. The expression in (17.6.23) may be written as

$$N_W |E_0|^2 \left[1 + \frac{2|M_W| \cos(2\omega_0 t + \lambda)}{N_W} \right], \quad \lambda = \arg[M_W E_0^2],$$

where the term in brackets must be positive. It follows that, for all t ,

$$N_W > 2|M_W| \cos(2\omega_0 t + \lambda). \quad (17.6.24)$$

We can therefore write (17.6.22) as the numerator multiplying the factor

$$\frac{1}{N_W |E_0|^2} [1 + A],$$

where A is an infinite expansion of powers of terms involving $e^{\pm 2i\omega_0 t}$. This expansion is convergent by virtue of the inequality (17.6.24). If we take the average of $F_d(t)$ over any time interval of duration $\frac{\pi}{\omega_0}$, it reduces to

$$\begin{aligned} F_{dc} &= \frac{N_{\mathcal{D}}}{N_W} = \frac{i|\omega_-|^2 K_{+-}(\omega_-, \omega_+)}{\omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)}, \\ F_{sc} &= 1 - F_{dc} = \frac{N_{\psi}}{N_W} \\ &= \frac{-i|\omega_-|^2 K_{+-}(\omega_-, \omega_+) + \omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)}{\omega_- \mathcal{M}_+(-\omega_+) - \omega_+ \mathcal{M}_+(\omega_-)}. \end{aligned} \quad (17.6.25)$$

17.6.1.3 Purely Sinusoidal Histories

For this case, the quantities $W(t)$ and $\mathcal{D}(t)$ diverge, as pointed out after (17.6.15) and (17.6.21). We can write an approximate version of (11.7.5) as

$$\begin{aligned}
 W(t) &= \{M_W, N_W\}, \\
 M_W &= \frac{1}{2} [G_0 + G'_+(\omega_0)] \\
 N_W &= G_0 + G'_c(\omega_0) - \omega_0 \frac{\partial}{\partial \omega_0} G'_c(\omega_0) - G'_s(\omega_0) \omega_0 \left(2t + \frac{1}{\eta}\right).
 \end{aligned}$$

In the limit $\eta \rightarrow 0$, the quantity N_W does not meet the criterion specified in Remark 17.6.1, so that $W(t)$ does not obey condition P4.

In this limit, where $\eta \rightarrow 0$, (17.6.11) and (17.6.12) become

$$\{M, N\} = ME_0^2 e^{2i\omega_0 t} + \overline{M} \overline{E_0}^2 e^{-2i\omega_0 t} + N|E_0|^2. \quad (17.6.26)$$

Relation (17.6.14) converges to a finite result of the form

$$T(t)\dot{E}(t) = \{i\omega_0 \mathcal{M}_+(\omega_0), 2H(\omega_0)\},$$

where (16.1.10) and (16.1.13) have been invoked. Also, (17.6.17) and (17.6.18) yield

$$\begin{aligned}
 M_\psi &= \frac{1}{2} \left\{ \mathcal{M}_+(\omega_0) + \frac{i\omega_0}{2} K_{+-}(\omega_0, -\omega_0) \right\}, \\
 N_\psi &= \mathcal{R}(\omega_0) - \omega_0 \frac{d}{d\omega_0} \mathcal{R}(\omega_0) + U(\omega_0), \\
 U(\omega_0) &= \frac{i\omega_0^2}{2} \left[-\frac{\partial}{\partial \omega_1} K_{+-}(\omega_1, \omega_2) + \frac{\partial}{\partial \omega_2} K_{+-}(\omega_1, \omega_2) \right] \Big|_{\omega_1=\omega_2=\omega_0},
 \end{aligned} \quad (17.6.27)$$

where $\mathcal{R}(\omega)$ is defined by (16.1.10). Finally, from (17.6.19) and (17.6.20), we deduce that

$$D(t) = \left\{ \frac{\omega_0^2}{2} K_{+-}(\omega_0, -\omega_0), 2H(\omega_0) \right\}, \quad (17.6.28)$$

where (17.5.18) has been used. Applying (17.6.13)₂ in the sinusoidal limit, one can show that (16.1.28) is obeyed.

Comparison with Special Cases

We now compare these results with previously given particular examples of sinusoidal histories. The minimum free energy is discussed in detail for such histories in Sect. 11.7. Precisely analogous formulae apply to all the $\psi_f(t)$. Thus, we have, in the notation (17.6.26), using the complex modulus given by (16.1.9), rather than $G'(\omega_0)$ or $\tilde{G}(\omega_0)$,

$$\psi_f(t) = \left\{ \frac{1}{2} \left[\mathcal{M}_+(\omega_0) + \frac{i}{\omega_0} \left[H_-^f(-\omega_0) \right]^2 \right], R(\omega_0) - \omega_0 \frac{d}{d\omega_0} R(\omega_0) + Q_f(\omega_0) \right\}, \quad (17.6.29)$$

where $Q_f(\omega)$ is given by

$$Q_f(\omega) = i \left[\frac{d}{d\omega} H_+^f(\omega) H_-^f(\omega) - H_+^f(\omega) \frac{d}{d\omega} H_-^f(\omega) \right] \geq 0, \quad \omega \in \mathbb{R}. \quad (17.6.30)$$

The rate of dissipation is given by (16.4.12) and (16.4.6). It can be shown that

$$K_f(t) = H_-^f(-\omega_0)E_0e^{i\omega_0t} + H_-^f(\omega_0)\overline{E_0}e^{-i\omega_0t},$$

yielding

$$D_f(t) = \{[H_-^f(-\omega_0)]^2, 2H(\omega_0)\} = \{[H_+^f(\omega_0)]^2, 2H(\omega_0)\}, \quad (17.6.31)$$

where (16.4.1) has been used.

We see that relations (17.6.29) and (17.6.31) are the special cases of (17.6.27) and (17.6.28) for $\omega_1\omega_2K_{+-}(\omega_1, \omega_2) = -2H_+^f(\omega_1)H_+^f(\omega_2)$. In particular, the quantity $Q_f(\omega)$ in (17.6.30) is equal to $U(\omega)$ in (17.6.27) for this choice of kernel.

17.6.1.4 Exponential Histories

This can be treated either by direct calculation, or as a special case of the general formulae of Sect. 17.6.1.2, where $\omega_0 \rightarrow 0$. We consider a history and current value $(E^t, E(t))$ given by (16.11.1) with $\omega_0 = 0$, so that

$$E(t) = E_e e^{\eta t}, \quad E^t(s) = E(t-s), \quad E_e = E_0 + \overline{E_0}.$$

The stress function, given by (17.6.10), has the form

$$T(t) = \mathcal{M}_+(-i\eta)E(t), \quad \mathcal{M}_+(-i\eta) = G_\infty + \eta\widetilde{G}_+(-i\eta), \quad (17.6.32)$$

where the forms of $\mathcal{M}_+(-i\eta)$ can be deduced from (16.1.9). This quantity is real. From (17.6.32) or as special cases of (17.6.14) and (17.6.15), we have

$$\begin{aligned} T(t)\dot{E}(t) &= \eta\mathcal{M}_+(-i\eta)E^2(t) = \frac{1}{2}\mathcal{M}_+(-i\eta)\frac{d}{dt}E^2(t), \\ W(t) &= \frac{1}{2}\mathcal{M}_+(-i\eta)E^2(t). \end{aligned} \quad (17.6.33)$$

Also, (17.6.16), (17.6.17), and (17.6.18) reduce to

$$\psi(t) = \frac{1}{2}[\mathcal{M}_+(-i\eta) + \frac{\eta}{2}K_{+-}(-i\eta, i\eta)]E^2(t). \quad (17.6.34)$$

The rate of dissipation and total dissipation are special cases of (17.6.19) and (17.6.21), given by

$$D(t) = -\frac{\eta^2}{2}K_{+-}(-i\eta, i\eta)E^2(t), \quad \mathcal{D}(t) = -\frac{\eta}{4}K_{+-}(-i\eta, i\eta)E^2(t). \quad (17.6.35)$$

The results for the various quadratic quantities above can be summarized in a simple formula. Putting $\omega_0 = 0$ in (17.6.11), we have

$$V(t) = V_0 e^{2\eta t}, \quad V_0 = ME_0^2 + \overline{M} \overline{E_0}^2 + N|E_0|^2.$$

It can be shown using (17.3.5), (17.3.11), and (17.3.19), relating, respectively, to $\psi(t)$, $D(t)$, and $W(t)$, that

$$M = \overline{M} = \frac{N}{2}, \quad (17.6.36)$$

for exponential histories. This relation must therefore hold true for $\mathcal{D}(t)$, by virtue of (16.1.29). Equation (17.6.36) can also be shown using various explicit formulae from (17.6.15) to (17.6.21). It gives that $V_0 = ME_e^2$ or

$$V(t) = ME^2(t). \quad (17.6.37)$$

Each result in (17.6.33)–(17.6.35) has the form (17.6.37) where, for example, if $M = M(\omega_-, \omega_+)$ in the general sinusoidal/exponential case, this is replaced by $M = M(-i\eta, i\eta)$. The property (17.6.37) was first noted in [16].

The quantities F_s and F_d , defined by (17.6.2), are time-independent and given by

$$F_s = \frac{\mathcal{M}_+(-i\eta) + \frac{\eta}{2}K_{+-}(-i\eta, i\eta)}{\mathcal{M}_+(-i\eta)}, \quad F_d = -\frac{\eta}{2} \frac{K_{+-}(-i\eta, i\eta)}{\mathcal{M}_+(-i\eta)}.$$

Note that

$$F_s = F_{sc}, \quad F_d = F_{dc},$$

where F_{sc} and F_{dc} are the quantities introduced in (17.6.25), with ω_{\pm} replaced by $\pm i\eta$, as in the comment after (17.6.37).

Various detailed expressions for step function and SE histories are presented in [18]. Plots of some of these functions are also presented.

17.7 Product Formulae in the Time and Frequency Domains

We now choose general histories and special forms of kernels, using results obtained in Sect. 17.5 to help determine new nonnegative rates of dissipation and from these to deduce new free energies.

In the time and frequency domains, we have the corresponding conditions (17.4.10) and (17.5.18), which constrain the choice of kernels for the rate of dissipation. This category is in fact very general and will be explored in this section.

The simplest method of creating nonnegative quadratic functionals is to assume that the relevant kernels have the form of sums of products.

Also, a family of free energy functionals is introduced, which is a generalization of the category discussed in Sect. 16.4 consisting of the minimum and related free energies.

It should be emphasized that all developments in the time and frequency domains are equivalent.

17.7.1 The Time Domain

Let us take

$$K(s, u) = - \sum_{i,j=1}^m A_{ij} k_i(s) k_j(u), \tag{17.7.1}$$

for some positive integer m , where it is assumed that all quantities $\int_0^\infty k_i(s) \dot{E}^t(s) ds$, $i = 1, 2, \dots, m$ exist, for the class of histories of interest. The matrix \mathbf{A} is assumed to be nonnegative. The rate of dissipation is given by

$$D(t) = \frac{1}{2} \int_0^\infty \int_0^\infty \sum_{i,j=1}^m \dot{E}^t(s) A_{ij} k_i(s) k_j(u) \dot{E}^t(u) ds du \geq 0. \tag{17.7.2}$$

We obtain from (17.4.9) that

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) \sum_{i,j=1}^m A_{ij} k_i(z+s) k_j(z+u) dz \dot{E}^t(u) ds du. \tag{17.7.3}$$

From (17.4.10), it follows that

$$\tilde{G}(s) = \int_0^\infty \sum_{i,j=1}^m A_{ij} k_i(z) k_j(z+s) dz. \tag{17.7.4}$$

The simplest case of (17.7.1) is where $m = 1$. Absorbing $\sqrt{A_{11}}$ into $k(s)$, we obtain

$$K(s, u) = -k(s)k(u), \quad D(t) = \frac{1}{2} \left[\int_0^\infty k(s) \dot{E}^t(s) ds \right]^2, \tag{17.7.5}$$

and

$$\tilde{G}(s, u) = \int_0^\infty k(z+s)k(z+u) dz,$$

giving

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) k(z+s) k(z+u) \dot{E}^t(u) ds du dz. \tag{17.7.6}$$

Relation (17.7.4) becomes

$$\tilde{G}(s) = \int_0^\infty k(z)k(z+s) dz. \tag{17.7.7}$$

The quantity $\tilde{G}(s)$ is the given relaxation function characterizing the material, while the free energy determined by (17.7.6) is one of (usually) many functionals that generate this quantity. Relation (17.7.7) can be regarded as a nonlinear integral equation for $k(\cdot)$ in terms of $\tilde{G}(s)$.

The quantity $k(s)$ determines $K(s, u)$ in accordance with (17.7.5)₁ and therefore the corresponding $D(t)$ and $\psi(t)$. We return to this case in Sect. 17.7.2,

Two further special cases will be considered, that where

$$A_{ij} = 1 \quad \text{or} \quad A_{ij} = \delta_{ij}, \quad i, j = 1, 2, \dots, m, \quad (17.7.8)$$

where δ_{ij} is the standard Kronecker delta notation. For (17.7.8)₁, relation (17.7.2) becomes

$$D(t) = \frac{1}{2} \left[\sum_{i=1}^m \int_0^\infty k_i(s) \dot{E}^t(s) ds \right]^2, \quad (17.7.9)$$

which is clearly nonnegative. It follows from (17.7.3) that the corresponding free energy has the form

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) \sum_{i,j=1}^m k_i(z+s) k_j(z+u) dz \dot{E}^t(u) ds du. \quad (17.7.10)$$

For example, consider the results of Sect. 16.9.1. Referring to (16.9.9), we see that, for $D_f(t)$, the quantity $k_i(s)$ in (17.7.9) is given by

$$k_i(s) = \frac{\sqrt{2} h_\infty R_i^f e^{-\alpha_i s}}{\alpha_i}, \quad i = 1, 2, \dots, n,$$

where $m = n$, so that (17.7.10) gives (16.9.7).

For (17.7.8)₂, we obtain

$$K(s, u) = - \sum_{i=1}^m k_i(s) k_i(u). \quad (17.7.11)$$

The rate of dissipation has the form

$$D(t) = \frac{1}{2} \sum_{i=1}^m \left[\int_0^\infty k_i(s) \dot{E}^t(s) ds \right]^2 \geq 0. \quad (17.7.12)$$

It follows from (17.7.3) that

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty \int_0^\infty \int_0^\infty \dot{E}^t(s) \sum_{i=1}^m k_i(z+s) k_i(z+u) dz \dot{E}^t(u) ds du. \quad (17.7.13)$$

Also, from (17.7.4),

$$\tilde{G}(s) = \int_0^\infty \sum_{i=1}^m k_i(z) k_i(z+s) dz. \quad (17.7.14)$$

Putting

$$k_i(s) = \sqrt{2\alpha_i G_i} e^{-\alpha_i s}$$

in (17.7.12) gives (17.4.20)₂ while (17.7.13) yields (17.4.20)₁, relating to the Dill free energy.

17.7.1.1 New Category of Free Energies: Time Domain

We now sketch a systematic approach to the construction of a new family of free energies. This can be developed only in general terms for the time domain representation. The frequency representation is considered in Sect. 17.7.2.1 below, and it emerges that one can give explicit formulae for the new free energies in that formalism.

Remark 17.7.1. Let us assume that $\tilde{G}(s)$ can be decomposed into m components $\tilde{G}_i(s)$, $i = 1, 2, \dots, m$, so that

$$\tilde{G}(s) = \sum_{i=1}^m \tilde{G}_i(s), \tag{17.7.15}$$

where each $\tilde{G}_i(s)$ is the relaxation function of a well-defined material, obeying the laws of thermodynamics, in particular (16.1.12). The term sub-material will be used in reference to each of these. The strain function is assumed to be the same in each sub-material.

For example, in the case of discrete-spectrum materials, $\tilde{G}(s)$ is given by (11.9.1). We could take $\tilde{G}_i(\omega)$ to be any partial sum of the terms in that expression, e.g.,

$$\tilde{G}_i(s) = \sum_{k=n_i}^{m_i} G_k e^{-\alpha_k s}, \quad n \geq m_i > n_i \geq 1. \tag{17.7.16}$$

The choice of terms in this relation need not reflect our original order.

We put

$$\tilde{G}_i(s) = \int_0^\infty k_i(z)k_i(z + s)dz, \quad i = 1, 2, \dots, m, \tag{17.7.17}$$

yielding a relation of the form (17.7.14). For each i , (17.7.17) can be regarded as a nonlinear integral equation for $k_i(s)$ in terms of the known quantity $\tilde{G}_i(s)$. These equations can be solved in the same way as (17.7.7) (see Sect. 17.7.2.1 below). The solutions yield the form of $K(s, u)$ as given by (17.7.11), and therefore allow us to determine $D(t)$ and $\psi(t)$.

17.7.2 The Frequency Domain

Referring to (17.5.1) and (17.7.1), we have

$$K_{+-}(\omega_1, \omega_2) = - \sum_{i,j=1}^m A_{ij}k_{i+}(\omega_1)k_{j-}(\omega_2) = - \sum_{i,j=1}^m A_{ij}\overline{k_{i-}}(\omega_1)k_{j-}(\omega_2), \tag{17.7.18}$$

where

$$k_{i-}(\omega) = \int_0^\infty k_i(s)e^{i\omega s}ds, \quad k_{i+}(\omega) = \overline{k_{i-}}(\omega). \tag{17.7.19}$$

Condition (17.5.18)₁ gives that

$$\sum_{i,j=1}^m A_{ij} \overline{k_{i-}}(\omega) k_{j-}(\omega) = 2 \frac{H(\omega)}{\omega^2}. \quad (17.7.20)$$

In the case where $m = 1$, we have

$$K_{+-}(\omega_1, \omega_2) = -k_+(\omega_1)k_-(\omega_2) \quad (17.7.21)$$

and relation (17.7.20) becomes

$$k_+(\omega)k_-(\omega) = |k_-(\omega)|^2 = 2 \frac{H(\omega)}{\omega^2}. \quad (17.7.22)$$

We solve (17.7.7) at this point and show that it is equivalent to (17.7.22). Substituting the inverse transforms of (17.7.19) into (17.7.7) and carrying out two time domain integrations yields

$$\begin{aligned} \widetilde{G}_+(\omega) &= -\frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{k_-(\omega_1)k_+(\omega_2)}{(\omega_1^- - \omega_2^+)(\omega^- - \omega_2^+)} d\omega_1 d\omega_2 \\ &= -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{k_+(\omega')k_-(\omega')}{\omega' - \omega^-} d\omega'. \end{aligned} \quad (17.7.23)$$

The choice ω_2^+ in the first form is dictated by the need for the time domain integrals to converge. The final form is obtained by integrating ω_1 over $\mathcal{Q}^{(+)}$. Taking the complex conjugate of (17.7.23)₂ and applying the Plemelj formulae give

$$\overline{\widetilde{G}_+(\omega)} + \widetilde{G}_+(\omega) = 2\widetilde{G}_c(\omega) = 2 \frac{H(\omega)}{\omega^2} = k_+(\omega)k_-(\omega) = |k_-(\omega)|^2, \quad (17.7.24)$$

which agrees with (17.7.22).

Relation (17.7.22) or (17.7.24) is of course the factorization problem for $H(\omega)$. The solution is given either by the factors (16.1.14), which yield the minimum free energy for all materials, or those given by (16.4.1) for materials with only isolated singularities. Thus, for some materials, the solution of (17.7.22) is non-unique. We put

$$k_-(\omega) = \sqrt{2} \frac{H_-^f(\omega)}{\omega}. \quad (17.7.25)$$

It follows from (17.7.21) that

$$K_{+-}(\omega_1, \omega_2) = -2 \frac{H_+^f(\omega_1)H_-^f(\omega_2)}{\omega_1\omega_2}. \quad (17.7.26)$$

Equation (17.7.26) yields the rate of dissipation $D_f(t)$ given by (16.4.17) and $\psi_f(t)$ of the form (16.4.15), both expressed in terms of \dot{E}_+^t with the aid of (16.1.17).

We now assume that \mathbf{A} is the unit matrix so that

$$K_{+-}(\omega_1, \omega_2) = - \sum_{i=1}^m \overline{k_{i-}}(\omega_1)k_{i-}(\omega_2). \quad (17.7.27)$$

Relations (17.5.7)₂ and (17.5.13) give

$$D(t) = \frac{1}{8\pi^2} \sum_{i=1}^m \int_{-\infty}^{\infty} |k_{i-}(\omega) \dot{E}_+^t(\omega)|^2 d\omega,$$

$$\psi(t) = \phi(t) + \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\overline{\dot{E}_+^t(\omega_1)} \sum_{i=1}^m \overline{k_{i-}(\omega_1)} k_{i-}(\omega_2) \dot{E}_+^t(\omega_2)}{\omega_1^+ - \omega_2^-} d\omega_1 d\omega_2.$$

Condition (17.5.18)₁ gives that

$$\sum_{i=1}^m \overline{k_{i-}(\omega)} k_{i-}(\omega) = \sum_{i=1}^m |k_{i-}(\omega)|^2 = 2 \frac{H(\omega)}{\omega^2}. \tag{17.7.28}$$

An immediate example of (17.7.27) satisfying (17.7.28) is obtained by taking $m = N$ and

$$k_{i-}(\omega) = k_{f-}(\omega) = \frac{\sqrt{2\lambda_f} H_-^f(\omega)}{\omega}, \tag{17.7.29}$$

giving

$$K_{+-}(\omega_1, \omega_2) = -2 \sum_{f=1}^N \lambda_f \frac{H_+^f(\omega_1) H_-^f(\omega_2)}{\omega_1 \omega_2}.$$

Other solutions of (17.7.28) may of course exist.

17.7.2.1 New Category of Free Energies: Frequency Domain

The developments in this section are the frequency domain version of those in Sect. 17.7.1.1. Here, we use (17.7.27) and (17.7.28) to determine a family of free energies, corresponding to (17.7.11) and (17.7.14) in Sect. 17.7.1.1.

It follows from Remark 17.7.1 that the quantity $H(\omega)$ can be decomposed into m components $H_i(\omega)$, $i = 1, 2, \dots, m$, corresponding to (17.7.15) so that

$$H(\omega) = \sum_{i=1}^m H_i(\omega), \tag{17.7.30}$$

where each $H_i(\omega)$ is related to $\widetilde{G}_i(s)$ in accordance with (16.1.13) and in particular is nonnegative for $\omega \in \mathbb{R}$. It is the quantity $H(\omega)$ for the sub-material with relaxation function $\widetilde{G}_i(s)$.

For example, in the case of discrete-spectrum materials, $H(\omega)$ is given by (11.9.2). We could take $H_i(\omega)$ to be any partial sum of the terms in that expression, *e.g.*,

$$H_i(\omega) = \omega^2 \sum_{k=n_i}^{m_i} \frac{\alpha_k G_k}{\alpha_k^2 + \omega^2}, \quad n \geq m_i > n_i \geq 1,$$

corresponding to (17.7.16).

In general, each $H_i(\omega)$ can be factorized as in (16.1.14) or, for a material with only isolated singularities, (16.2.9). Thus, we write

$$H_i(\omega) = H_{i+}^f(\omega)H_{i-}^f(\omega), \quad H_{i\pm}^f(\omega) = H_{i\mp}^f(-\omega) = \overline{H_{i\pm}^f(\omega)}.$$

For materials with only isolated singularities, the factorization indicated by the superscript f will vary with the subscript i .

Starting from (17.7.17) and applying the procedure leading to (17.7.24) and (17.7.25) for each i , we obtain (17.7.28) by virtue of (17.7.30). Relation (17.7.25) for each i and (17.7.30) can be written as

$$k_{i-}(\omega) = \sqrt{2} \frac{H_{i-}^f(\omega)}{\omega},$$

$$\sum_{i=1}^m \overline{k_{i-}(\omega)} k_{i-}(\omega) = 2 \sum_{i=1}^m \frac{H_{i+}^f(\omega)H_{i-}^f(\omega)}{\omega^2} = 2 \frac{H(\omega)}{\omega^2},$$

for the range of possible choices of f corresponding to each i , where $H_{i\pm}^f(\omega)$ are a particular pair of factors of $H_i(\omega)$. Thus, we have

$$K_{+-}(\omega_1, \omega_2) = -2 \sum_{i=1}^m \frac{H_{i+}^f(\omega_1)H_{i-}^f(\omega_2)}{\omega_1\omega_2}. \tag{17.7.31}$$

The superscript f will now be dropped to simplify notation.

If (17.7.31)₁ is inserted into (17.5.7) expressed in terms of $E_{r+}^t(\omega)$ by means of (16.1.17), we obtain

$$D(t) = \sum_{i=1}^m |K_i(t)|^2, \tag{17.7.32}$$

$$K_i(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} H_{i-}(\omega)E_{r+}^t(\omega)d\omega.$$

These relations are analogous to (16.4.12) and (16.4.6) with $H_{i-}(\omega)$ playing the role of $H_-^f(\omega)$. Substituting (17.7.31)₁ into (17.5.13)₂ gives a sum of terms identical to (16.4.15) but with $H_{i\pm}$ replacing H_{\pm}^f . Substituting (17.7.31)₁ into (17.5.17)₂ yields a sum of terms of the form (16.4.16) with $H_{i\pm}$ rather than H_{\pm}^f . Again, each term can be put in the form (16.4.11) with the above replacements. The free energy and total dissipation can therefore be written as

$$\psi(t) = \phi(t) + \frac{1}{2\pi} \sum_{i=1}^m \int_{-\infty}^{\infty} |p_{i-}^t(\omega)|^2 d\omega, \quad \mathcal{D}(t) = \sum_{i=1}^m \int_{-\infty}^{\infty} |p_{i+}^t(\omega)|^2 d\omega,$$

where

$$p_{i-}^t(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_{i-}(\omega')E_{r+}^t(\omega')}{\omega' - \omega^+} d\omega',$$

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

These new free energies clearly obey (16.1.26). The rate of dissipation is nonnegative, by virtue of (17.7.32). Also, we can demonstrate that (16.1.25) holds by an argument analogous to that in Proposition 11.2.2.

The ordering of these free energy functionals is discussed in some detail in [162].

17.8 Approximation of a Discrete-Spectrum Material by a Day Functional

This and the following section of the present chapter deal with topics that are not closely related to those in earlier sections.

For materials with relaxation function containing one decaying exponential, the associated Day functional is the physical free energy. For general discrete-spectrum materials, we seek a best fit of the relaxation function with one decaying exponential to that for the general case.

For the case $n = 1$, the relations (16.3.13) and (16.3.15) reduce to the formulae for the Day free energy and rate of dissipation (see (10.2.15), (16.9.10) and [87]). A relaxation function with only one decaying exponential, has the form (see (10.2.15), (16.9.10), and (16.9.11))

$$G_D(t) = G_\infty + G_d e^{-\alpha t}, \quad G_d = G_0 - G_\infty. \quad (17.8.1)$$

This behavior has, in some contexts, been referred to as the standard linear model [167]. The complex modulus, defined by (16.1.9)₂, is given by

$$\mathcal{M}_+(\omega) = G_\infty + i\omega \sum_{i=1}^n \frac{G_i}{\alpha_i + i\omega},$$

so that for $n = 1$

$$\mathcal{M}_+(\omega) = \frac{(\alpha + i\omega)G_\infty + i\omega G_d}{\alpha + i\omega}. \quad (17.8.2)$$

By virtue of (16.3.14) and (16.3.15)₄, we must have

$$C_{11} = G_d, \quad \Gamma_{11} = 2\alpha G_d.$$

The Day free energy functional is given by

$$\psi_D(t) = \phi(t) + \frac{G_d}{2} e_1^2(t), \quad (17.8.3)$$

in terms of $e_1(t)$ defined by (16.3.12). The corresponding rate of dissipation is

$$D_D(t) = \alpha G_d e_1^2(t).$$

From (17.6.15) and (17.8.2), we can determine M_W and N_W for this case. In particular,

$$N_W = G_\infty + G_d \frac{(\omega_0^2 + \eta^2)(\alpha + \eta)}{\eta[(\alpha + \eta)^2 + \omega_0^2]}.$$

The kernels (17.4.14) reduce to

$$\widetilde{G}(s, u) = G_d e^{-\alpha(s+u)}, \quad K(s, u) = -2\alpha G_d e^{-\alpha(s+u)}, \quad (17.8.4)$$

and (17.5.21) becomes

$$\begin{aligned} \widetilde{G}_{+-}(\omega_1, \omega_2) &= \frac{G_d}{(\alpha + i\omega_1)(\alpha - i\omega_2)}, \\ K_{+-}(\omega_1, \omega_2) &= -\frac{2\alpha G_d}{(\alpha + i\omega_1)(\alpha - i\omega_2)}, \end{aligned}$$

which yield explicit functions for $M_{\mathcal{D}}$ and $N_{\mathcal{D}}$, given by (17.6.21). Thus, we obtain that

$$M_{\mathcal{D}} = \frac{iG_d}{2} \frac{(w_0 - i\eta)\alpha}{(\alpha + \eta + i\omega_0)^2}, \quad N_{\mathcal{D}} = G_d \frac{\alpha(\omega_0^2 + \eta^2)}{\eta[(\alpha + \eta)^2 + \omega_0^2]}.$$

Relations (16.9.9) and (16.9.7) are particular cases of the general formulae (16.3.13) and (16.3.15), and must have the same limit for $n = 1$. This can be seen by noting that

$$H_\infty = -G'(0) = \alpha G_d,$$

and

$$R_1^1 = -\alpha,$$

which follows from the generalization of (11.9.7) to R_i^f , for $n = 1$.

The fundamental point made in this chapter is that a material with memory is completely characterized by choosing $K(s, u)$ rather than the relaxation function. However, for the $n = 1$ case, specifying the relaxation function parameters fixes uniquely the kernel $K(s, u)$ and therefore determines the material completely. Thus, the set \mathcal{K} for $n = 1$ is a singleton given by (17.8.4)₂, and there is only one material with the constitutive relation generated by the relaxation function (17.8.1), with parameters as specified.

Remark 17.8.1. If a material behavior can be adequately simulated by one decay constant α , together with coefficients G_∞ and G_d , then $\psi_{\mathcal{D}}(t)$, given by (17.8.3), is the physical free energy for that material.

We now seek the Day relaxation function which is closest to the actual relaxation function for the materials in \mathcal{K} .

The α_i , $i = 1, 2, \dots, n$, in (11.9.1) are given by (16.11.4), while the G_i , $i = 1, 2, \dots, n$, are determined by the assumption that the G_i are all equal [18]. We choose G_0 , G_∞ and α such that the resulting $n = 1$ relaxation function approximates (11.9.1) as closely as possible.

We choose G_0 and G_∞ to be the same for the materials with relaxation function given by (11.9.1) and (17.8.1), respectively.

Choosing the optimal value of α is somewhat more difficult. Consider

$$\begin{aligned} f(\alpha) &= \frac{1}{G_d^2} \int_0^\infty [G_D(s) - G(s)]^2 ds \\ &= \frac{1}{G_d^2} \int_0^\infty \left[G_d e^{-\alpha s} - \sum_{i=1}^n G_i e^{-\alpha_i s} \right]^2 ds, \end{aligned} \tag{17.8.5}$$

which is a $L^2(\mathbb{R}^+)$ norm of the difference between the relaxation functions for the Day case and that in (11.9.1). Then, we put

$$f_m = \min_{\alpha > 0} f(\alpha), \tag{17.8.6}$$

and this minimum is achieved at α_d , so that

$$f(\alpha_d) = f_m \leq f(\alpha) \quad \forall \alpha \in \mathbb{R}^+. \tag{17.8.7}$$

The quantity α_d is the inverse time decay constant that will be used in the Day free energy and dissipation. The function $f(\alpha)$, given by (17.8.5), can be explicitly calculated. Let us replace α by α_0 . Then

$$\begin{aligned} f(\alpha_0) &= \sum_{i,j=0}^n \frac{c_i c_j}{\alpha_i + \alpha_j}, \quad \alpha_0 \in (0, 1], \\ c_i &= \begin{cases} 1, & i = 0, \\ -\frac{G_i}{G_d}, & i = 1, 2, \dots, n. \end{cases} \end{aligned} \tag{17.8.8}$$

This can be written in the form

$$f(\alpha_0) = \frac{1}{2\alpha_0} + 2 \sum_{i=1}^n \frac{c_i}{\alpha_0 + \alpha_j} + \sum_{i,j=1}^n \frac{c_i c_j}{\alpha_i + \alpha_j}, \tag{17.8.9}$$

so that

$$f'(\alpha_0) = -\frac{1}{2\alpha_0^2} - 2 \sum_{i=1}^n \frac{c_i}{(\alpha_0 + \alpha_j)^2}.$$

Thus, the α_0 satisfying (17.8.7) is the solution of the equation

$$1 + 4 \sum_{i=1}^n \frac{c_i \alpha_0^2}{(\alpha_0 + \alpha_j)^2} = 0. \tag{17.8.10}$$

The solution gives a minimum value of $f(\alpha)$ if $f''(\alpha_0) > 0$. This quantity α_0 is equal to α_d .

It makes little difference what value of n is adopted. We choose $n = 5$ as an example. The numerical values of α_r , $r = 1, 2, 3, 4, 5$, given by (16.11.4), are 0.0718, 0.2679, 0.5359, 0.8038 and 1.0.

The appropriate Day relaxation function is determined by (17.8.5) - (17.8.7) where $f(\alpha)$ has the form (17.8.9). Since the G_i are all equal, (17.8.8)₂ becomes

$$c_i = \begin{cases} 1, & i = 0, \\ -\frac{1}{n}, & i = 1, 2, \dots, n, \end{cases}$$

with the aid of (16.11.6) and (17.8.1)₂. We look for a solution to (17.8.10) where $\alpha_0 \in (0, 1]$. This is equal to 0.3225 [18], with optimum choice $f(\alpha_d) = f_m = 0.0968$.

Thus, an approximate form of the physical free energy for all the materials associated with the relaxation function $\tilde{G}(s)$ of the form (11.9.1), with parameter values as stated, is given by (17.8.3) with $\alpha_1 = \alpha_d$. There are in general many such materials so the approximation is probably not very accurate in most cases.

17.9 Single-Integral Free Energies in Terms of I^t Derivatives

Single-integral free energy functionals that are expressible as quadratic forms of the state functional I^t (see (16.5.1)) are considered in this section. The discussion is based on [163].

This form is shown to include the functional ψ_F . There is also, however, a further category of functionals of this kind for materials with non-singleton minimal states. These latter functionals are difficult to construct, since basic inequalities relating to thermodynamics must be explicitly imposed; they are therefore not so useful for practical applications, in contrast to ψ_F .

The following notation will be useful:

$$I_k^t(\tau) = \frac{d^k}{d\tau^k} I^t(\tau), \quad k = 1, 2, \dots \tag{17.9.1}$$

Then,

$$I_1^t(\tau) = \int_0^\infty G'(\tau + u) \dot{E}^t(u) du, \quad I_2^t(\tau) = \int_0^\infty G''(\tau + u) \dot{E}^t(u) du. \tag{17.9.2}$$

Also,

$$\frac{\partial}{\partial t} I_1^t(s) = G'(s) \dot{E}(t) + I_2^t(s), \quad \frac{\partial}{\partial t} I_2^t(s) = G''(s) \dot{E}(t) + I_3^t(s). \tag{17.9.3}$$

Just as in (16.5.2), we have

$$\lim_{\tau \rightarrow \infty} I_k^t(\tau) = 0, \quad k = 1, 2, 3, \dots \tag{17.9.4}$$

Consider the functional

$$\psi(t) = \phi(t) + \frac{1}{2} \int_0^\infty L(\tau) [I_1^t(\tau)]^2 d\tau. \tag{17.9.5}$$

This quantity is assumed to be a free energy. We now explore the constraints on $L(\tau)$ imposed by this requirement.

The relation (16.1.28) must hold. Using (16.1.31), (17.9.3)₁, and (17.9.4), we deduce that

$$\begin{aligned}\dot{\psi}(t) &= \dot{E}(t) \left[T_e(t) + \int_0^\infty G'(\tau)L(\tau)I_1'(\tau)d\tau \right] \\ &\quad + \int_0^\infty I_2'(\tau)L(\tau)I_1'(\tau)d\tau \\ &= T(t)\dot{E}(t) - \frac{1}{2}L(0)[I_1'(0)]^2 - \frac{1}{2} \int_0^\infty L'(\tau)[I_1'(\tau)]^2 d\tau,\end{aligned}$$

provided that the condition

$$\int_0^\infty G'(\tau)L(\tau)I_1'(\tau)d\tau = T(t) - T_e(t)$$

holds. With the help of (16.1.3), (16.5.3), and (17.9.2)₁, this can be written as

$$\begin{aligned}\int_0^\infty [G'(\tau)L(\tau) + 1]I_1'(\tau)d\tau \\ = \int_0^\infty \int_0^\infty [G'(\tau)L(\tau) + 1]G'(\tau + u)\dot{E}'(u)d\tau du = 0,\end{aligned}$$

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

$$\int_0^\infty G'(\tau + u)f(\tau)d\tau = 0 \quad \forall u \in \mathbb{R}^+, \quad f(\tau) = G'(\tau)L(\tau) + 1. \quad (17.9.6)$$

An alternative pathway to (17.9.6) is to express (17.9.5) in the form (17.3.5) with

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

and to impose the constraint (17.3.9), written in terms of $\tilde{G}(u)$. Condition (17.9.6) has the same form as (16.5.4), leading to

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

where $J_+(\omega)$ is an unknown function, analytic in $\Omega^{(-)}$. This corresponds to (16.5.7).

If the material has only isolated singularities, there are many nontrivial solutions of (17.9.6) given by a form similar to (16.5.15), as shown in [163].

If the material has branch cut singularities, then $f(\tau) = 0$, $\tau \in \mathbb{R}^+$ is the only solution of (17.9.6), so that

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

and the only possibility for a free energy given by a single-integral quadratic form is the quantity ψ_F (see Sect. 10.1.3). In the scalar theory, this functional and the associated rate of dissipation have the forms

$$\psi_F(t) = \phi(t) - \frac{1}{2} \int_0^\infty \frac{[I_1^t(\tau)]^2}{G'(\tau)} d\tau, \quad (17.9.7)$$

and

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

These quantities are nonnegative and $\psi_F(t)$ is a valid free energy if conditions (17.3.4) hold, not only for materials with branch point singularities, but for all materials. It is a relatively simple functional, convenient for applications.

The case of double integral quadratic forms is studied in depth in [163]. It is shown that the only such form that is a free energy is that for the minimum free energy discussed in Sect. 12.2.