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Free Energies for Nonlinear Materials with Memory

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Abstract
An exploration of representations of free energies and associated rates of dissipation for a broad class of nonlinear viscoelastic materials is presented in this work. Also included are expressions for the stress functions and work functions derivable from such free energies. For simplicity, only the scalar case is considered. Certain standard formulae are generalized to include higher power terms.

It is shown that the correct initial procedure in this context is to specify the rate of dissipation as a positive semi-definite functional and then to determine the free energy from this, rather than the other way around, which would be the traditional approach.

Particularly detailed versions of these formulae are given for the model with two memory contributions in the free energy, the first being the well-known quadratic functional leading to constitutive relations with linear history terms, while the second is a quartic functional yielding a cubic term for the stress function memory dependence. Also, the discrete spectrum model, for which each memory kernel is a sum of exponentials, is generalized from the quadratic functional representation for the free energy to that with the quartic functional included.

Finally, a model is considered, allowing functional power series with an infinite number of terms for the free energy, rate of dissipation and stress function.

1 Introduction

We consider a material with memory, where the independent field variable will be referred to as the strain function. It is taken to be a scalar quantity, for simplicity.

The general representation of a free energy of this material is a functional of the history of strain and a function of the current strain. We assume that this functional can be expanded as a finite or infinite functional Taylor expansion in the history of strain. The most general

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expansion of this kind has a dependence on the current strain in each kernel of the expansion. This dependence is neglected in the model considered here. The stress function is derivable from the free energy.

What we are dealing with in general is a nonlinear viscoelastic material. The linear memory/quadratic free energy model will be referred to as the linear model. Since the general formulae are quite complicated, the case involving one extra term beyond the linear model will be stated in full, including the linear model terms.

The results presented, or generalizations of these results to tensor form, should have practical applications in the context of numerical analysis of the mechanical behaviour of nonlinear materials with memory. Also, re-interpretation of the strain and stress functions as other physical quantities, combined in some cases with one or two minor changes, broadens the application range to include other thermodynamic systems, such as heat conductors and electromagnetic materials.

Relations within an equation number are referred to by counting the number of $=$, $<$, $>$ etc.

Thermodynamical constraints [1] on the theory are not discussed in this work. This is an important topic, requiring separate investigation.

2 Properties of Kernels

The current value of the strain function is $E(t)$ while the strain history and some relative histories are given by

$$
\begin{aligned}
E^t(s) &= E(t-s), \quad E_r^t(s) = E^t(s) - E(t), \\
E_r^u(s) &= E^u(s) - E(u), \quad E_r(s) = E(s) - E(t), \quad s \in \mathbb{R}^+.
\end{aligned}
\tag{2.1}
$$

Equation $(2.1)_3$ differs from $(2.1)_2$ only by a change of notation, but is included to emphasize that the relative strain is not always defined with respect to the current time t. The simple property

$$
\frac{\partial E_r^t(s)}{\partial E(t)} = -1
\tag{2.2}
$$

will be used later. It is assumed here that

$$
\lim_{s \to \infty} E^t(s) = \lim_{u \to -\infty} E(u) = 0,
\tag{2.3}
$$

which simplifies certain formulae. Note also that

$$
\dot{E}^t(u) = \frac{\partial}{\partial t} E^t(u) = -\frac{\partial}{\partial u} E^t(u) = -\frac{\partial}{\partial u} E_r^t(u).
\tag{2.4}
$$

The stress function is given by $T(t) = \tilde{T}(E^t, E(t))$, while we denote a particular free energy at time t by $\psi(t) = \tilde{\psi}(E^t, E(t))$, where $\tilde{T}(E^t, E(t))$ and $\tilde{\psi}(E^t, E(t))$ are understood to be functionals of E^t and functions of $E(t)$. Certain properties of free energies were derived in [2] and used to characterize such quantities in [3–5] and elsewhere. They have been referred to as the Graffi [6] definition of (or conditions for) a free energy and are given as follows. Let $\psi(t) = \tilde{\psi}(E^t, E(t))$ be a free energy. Then

P1:

$$\frac{\partial}{\partial E(t)}\tilde{\psi}(E^t, E(t)) = \frac{\partial}{\partial E(t)}\psi(t) = T(t).$$ (2.5)

P2: For any history E^t

$$\tilde{\psi}(E^t, E(t)) \geq \tilde{\phi}(E(t)) \text{ or } \psi(t) \geq \phi(t),$$ (2.6)

where $\phi(t) > 0$ is the equilibrium value of the free energy $\psi(t)$, defined as

$$\tilde{\phi}(E(t)) = \phi(t) = \tilde{\psi}(E^t, E(t)), \quad E^t(s) = E(t) \ \forall \ s \in \mathbb{R}^+.$$

Thus, equality in (2.6) is achieved for equilibrium conditions. Observe that the classical elastic energy $\phi(t)$ is always taken to be positive so that, from (2.6), the quantity $\psi(t)$ also has this property.

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

$$\dot{\psi}(t) + D(t) = T(t)\dot{E}(t),$$ (2.7)

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

The basic condition is P3. Relations P1 and P2 follow from P3.

Integrating (2.7) over $(-\infty, t]$ yields that

$$\psi(t) + \mathcal{D}(t) = W(t), \qquad \mathcal{D}(t) \geq 0,$$
$$\mathcal{D}(t) = \int_{-\infty}^{t} D(u)du, \quad W(t) = \int_{-\infty}^{t} T(u)\dot{E}(u)du.$$ (2.8)

The quantity $W(t)$ is the work function, while $\mathcal{D}(t)$ is the total dissipation resulting from the entire history of deformation of the body. It is assumed that the integrals in (2.8) are finite. In particular, we must have

$$\lim_{t \to -\infty} W(t) = 0,$$ (2.9)

with a similar assumption for $\mathcal{D}(t)$. The time derivative of $\tilde{\psi}(E^t, E(t))$ consists of the ordinary time derivative of the $E(t)$ dependence, giving, with the aid of (2.5),

$$T(t)\dot{E}(t) = \dot{W}(t),$$ (2.10)

and a functional derivative of the history dependence E^t, which yields the dissipation. Note that (2.10) follows from (2.8)$_4$.

Let us now briefly demonstrate that the work function also obeys P1, using a somewhat modified version of the argument in [2], and P2. We can write

$$\dot{W}(t) = \frac{\partial}{\partial E(t)}\widetilde{W}(E^t, E(t))\dot{E}(t) + \delta\widetilde{W},$$ (2.11)

where the rightmost term is a Fréchet differential of $\widetilde{W}$, defined within a suitable Hilbert space (for example [1], page 104). Thus, (2.10) can be written in the form

$$\left[\frac{\partial}{\partial E(t)} \widetilde{W}(E^t, E(t)) - \widetilde{T}(E^t, E(t)) \right] \dot{E}(t) = -\delta \widetilde{W}. \tag{2.12}$$

The quantity $\dot{E}(t)$ can take arbitrary values, so that (2.5) or P1 must hold for $\tilde{\psi}$ replaced by $\widetilde{W}$. Thus, we have

$$\frac{\partial}{\partial E(t)} \psi(t) = \frac{\partial}{\partial E(t)} W(t) = T(t), \tag{2.13}$$

giving

$$\widetilde{\mathcal{D}}(E^t, E(t)) = \widetilde{\mathcal{D}}(E^t). \tag{2.14}$$

It follows that

$$\frac{\partial}{\partial E(t)} \mathcal{D}(t) = 0. \tag{2.15}$$

Also, the quantity $\delta \widetilde{W}$ must vanish.

Note that $(2.8)_1$ implies

$$W(t) \geq 0. \tag{2.16}$$

2.1 Kernels of Free Energy Terms

The following functions are introduced:

$$G^{(k)}(\mathbf{u}^{(k)}), \quad \mathbf{u}^{(k)} = (u_1, u_2, \ldots, u_k) \in (\mathbb{R}^+)^k, \quad k = 1, 2, \ldots, N. \tag{2.17}$$

The quantity N is a positive integer, which may be infinite. If it is infinite, convergence assumptions must be included for the series involved. The superscript on G indicates the total number of arguments. We shall argue below that, for even k, these may be the kernels of a free energy, while for odd k, a particular choice of these quantities may define the stress function derived from the free energy (see (2.5)).

The quantities $G^{(k)}$ $k = 1, 2, \ldots, N$ and related functions introduced below first enter the model by their occurrence in integrals of the form

$$\int_0^\infty G^{(k)}(u_1, u_2, \ldots, u_k) f(u_1) f(u_2) \ldots f(u_k) du_1 du_2 \ldots du_k$$

$$= \int_0^\infty G^{(k)}(\mathbf{u}^{(k)}) \prod_{i=1}^{k} f(u_i) d\mathbf{u}^{(k)}, \tag{2.18}$$

$$d\mathbf{u}^{(k)} = du_1 du_2, \ldots, du_k, \quad k = 1, 2, \ldots, N,$$

where the single integral sign here and below is understood to mean as many integral signs as there are du_1, du_2 etc. The function $f(u)$, which is always related to the strain history,

can be chosen arbitrarily, subject to the requirement that the integral exists. Note that

$$\int_0^\infty G^{(k)}(u_1, u_2, \ldots, u_k) f(u_1) f(u_2) \ldots f(u_k) du_1 du_2 \ldots du_k$$
$$= \int_0^\infty G^{(k)}(u_2, u_1, \ldots, u_k) f(u_1) f(u_2) \ldots f(u_k) du_1 du_2 \ldots du_k, \tag{2.19}$$

which follows by using the standard device of renaming integration variables. A similar property holds for any permutation of $u_1, u_2, \ldots, u_k$. The important property here is the complete symmetry of the product of $f(u_i)$. Thus, only the totally symmetric part of the kernel contributes to the integral. For simplicity, we assume that

$$G^{(k)}(u_1, u_2, \ldots, u_k) = G^{(k)}(u_2, u_1, \ldots, u_k), \tag{2.20}$$

and similarly for any other permutation. In other words, we take $G^{(k)}$ $k = 1, 2, \ldots, N$ and similar related quantities to be completely symmetric in all their arguments.

For odd k, the functional of $f(u)$ given by (2.18) changes sign if $f(u)$ is replaced by $-f(u)$, so that it cannot be positive definite or semi-definite for all choices of $f(u)$. If k is even, then this non-negativity property can hold, provided certain restrictions are imposed on the kernel.

We only consider free energies consisting of terms with even k; the constraints on the kernels to guarantee non-negativity are assumed to hold. Each term separately will be non-negative. Equation (2.5) then gives that the stress function will only consist of terms with odd k.

It is assumed that the quantities $G^{(k)}(\mathbf{u}^{(k)})$, similar kernels introduced below and indeed the strain histories, have differentiability properties as required in the various contexts discussed in this work.

The constants $G_\infty^{(k)}$ are given by

$$G_\infty^{(k)} = \lim_{u_j \to \infty} G^{(k)}(u_1, u_2, \ldots, u_k), \tag{2.21}$$

where j is any integer in the set $\{1, 2, \ldots, k\}$. The fact that this quantity is the same for every j is an expression of the complete symmetry of the dependence of $G^{(k)}$ on its parameters. We illustrate this with the case $k = 2$, where $G^{(2)}(u_1, u_2)$ is converging to let us say G_1 if the first argument is very large and G_2 if the second is very large. The symmetry property $G^{(2)}(u_1, u_2) = G^{(2)}(u_2, u_1)$ gives that $G_2 = G_1$.

The quantities $G_\infty^{(k)}$ are non-negative. Let us define

$$\widetilde{G}^{(k)}(\mathbf{u}^{(k)}) = G^{(k)}(\mathbf{u}^{(k)}) - G_\infty^{(k)},$$
$$\mathcal{G}^{(k)}(\mathbf{u}^{(k)}) = G_{123\ldots k}^{(k)}(\mathbf{u}^{(k)}), \quad k = 1, 2, \ldots, N, \tag{2.22}$$

where a subscripted integer j indicates partial differentiation with respect to the corresponding u_j. Thus

$$\mathcal{G}^{(k)}(\mathbf{u}^{(k)}) = \partial_1 \partial_2 \ldots \partial_k G^{(k)}(\mathbf{u}^{(k)}), \quad k = 1, 2, \ldots, N, \tag{2.23}$$

where the operator ∂_j is the partial derivative $\frac{\partial}{\partial u_j}$.

The convergence of the integral (2.19)$_1$ is better at large u_j if $G^{(k)}(u_1, u_2, \ldots, u_k)$ is replaced by $\widetilde{G}^{(k)}(u_1, u_2, \ldots, u_k)$.

Consider the function space $\mathcal{F}^{(k)}$, where k is even, with a norm

$$\mathcal{N}^{(k)}(f) = \int_0^\infty \widetilde{G}^{(k)}(\mathbf{u}^{(k)}) \prod_{i=1}^k f(u_i) d\mathbf{u}^{(k)} \geq 0, \qquad \mathcal{N}^{(k)}(f) < \infty. \qquad (2.24)$$

This is a non-negative, finite quantity, as indicated. We assume that the function f, which in this context is always related to strain history, belongs to the function space

$$\mathcal{F}(f) = \mathcal{F}^{(0)} \cup \mathcal{F}^{(2)} \cdots \cup \mathcal{F}^{(N)}, \qquad (2.25)$$

where N is even and $\mathcal{F}^{(0)}$ contains functions without history dependence, specifically the quantities $\phi(t)$, defined by (3.3) below, with $E(t)$ replaced by $f(t)$.

2.2 The Kernels of the Rate of Dissipation Terms

We also define the functions

$$\begin{aligned}
K^{(k)}(\mathbf{u}^{(k)}) &= \sum_{i=1}^k \partial_i G^{(k)}(\mathbf{u}^{(k)}), \\
\mathcal{K}^{(k)}(\mathbf{u}^{(k)}) &= \sum_{i=1}^k \partial_i \mathcal{G}^{(k)}(\mathbf{u}^{(k)}), \quad k = 2, 4, \ldots, 2N,
\end{aligned} \qquad (2.26)$$

which will be shown to be the negative of the kernels making up the rate of dissipation $D(t)$, introduced in (2.7). These kernels are defined only for the positive even integers. They have the property that

$$K^{(k)}(\mathbf{u}^{(k)}), \mathcal{K}^{(k)}(\mathbf{u}^{(k)}) \to 0 \text{ for every parameter } u_i \to \infty, \quad i = 1, 2, \ldots, k, \qquad (2.27)$$

where $k = 2, 4, \ldots, 2N$.

A difficulty in constructing free energy functionals arises in making choices that ensure nonnegative functional forms both for the free energy and for the rate of dissipation. A method, proposed in the context of the linear model [7], which renders this task more straightforward, is generalized below to higher terms. Instead of constructing the free energy and determining from this the rate of dissipation, which may not have the required nonnegativity, the procedure is reversed, which guarantees a satisfactory free energy functional [7] (see also [1], pg. 394). One chooses a nonnegative functional for the rate of dissipation. Formulae are presented below which give the associated free energy functional in terms of the dissipation rate kernel. It emerges that the resulting free energy has the required nonnegativity property.

Proposition 2.1 *Let us assume that we know the form of the quantities $K^{(k)}(\mathbf{u}^{(k)})$ and that they have the required nonnegativity property, namely*

$$-\int_0^\infty K^{(k)}(\mathbf{u}^k) \prod_{i=1}^k f(u_i) d\mathbf{u}^k \geq 0, \quad k = 2, 4, \ldots, 2N, \qquad (2.28)$$

for arbitrary f. Then the kernels $G^{(k)}(\mathbf{u}^{(k)})$ are determined by

$$\widetilde{G}^{(k)}(\mathbf{u}^{(k)}) = - \int_0^\infty K^{(k)}(\mathbf{u}^{(k)} + \mathbf{z}^{(k)})dz, \quad k = 2, 4, \ldots, 2N,$$

$$\mathbf{z}^{(k)} = (z, z, \ldots, z) \in (\mathbb{R}^+)^k,$$

(2.29)

and they have the required nonnegativity properties.

Proof It follows from (2.29) that

$$\sum_{i=1}^k \partial_i G^{(k)}(\mathbf{u}^{(k)}) = - \int_0^\infty \frac{d}{dz} K^{(k)}(\mathbf{u}^{(k)} + \mathbf{z}^{(k)})dz = K^{(k)}(\mathbf{u}^{(k)}), \quad (2.30)$$

which is (2.26). We have

$$\int_0^\infty K^{(k)}(\mathbf{u}^{(k)} + \mathbf{z}^{(k)}) \prod_{i=1}^k f(u_i)d\mathbf{u}^k = \int_z^\infty K^{(k)}(\mathbf{v}^k) \prod_{i=1}^k f(v_i - z)d\mathbf{v}^k. \quad (2.31)$$

Let us put

$$F(v, z) = \begin{cases} f(v - z), & v \geq z, \\ 0, & 0 \leq v < z, \end{cases} \quad (2.32)$$

for arbitrary choices of $f(u)$. Then,

$$\int_0^\infty \widetilde{G}^{(k)}(\mathbf{u}^{(k)}) \prod_{i=1}^k f(u_i)d\mathbf{u}^k = - \int_0^\infty dz \left\{ \int_0^\infty K^{(k)}(\mathbf{v}^k) \prod_{i=1}^k F(v_i, z)d\mathbf{v}^k \right\} \geq 0, \quad (2.33)$$

by virtue of (2.28). It follows that $\widetilde{G}^{(k)}(\mathbf{u}^{(k)})$ has the required non-negativity property. $\quad\square$

There are two equivalent alternatives for the developments outlined below, the first being to use $\widetilde{G}^{(k)}(\mathbf{u}^{(k)})$, $K^{(k)}(\mathbf{u}^{(k)})$, $\dot{E}^t(s)$ and the second to use $\mathcal{G}^{(k)}(\mathbf{u}^{(k)})$, $\mathcal{K}^{(k)}(\mathbf{u}^{(k)})$, $E_r^t(s)$. Both have been widely adopted in discussing the minimum and related free energies for linear constitutive materials. In the present work, we will mainly present formulae in both notations. Moving from one alternative to the other involves a series of integrations by parts.

We can in fact choose either alternative for each parameter u_i, rather than fix on the same choice for all u_i, as in (3.1), below. For example, for u_i, we could switch from $\widetilde{G}^{(k)}(\mathbf{u}^{(k)})$, $K^{(k)}(\mathbf{u}^{(k)})$, $\dot{E}^t(u_i)$ to $\partial_i G^{(k)}(\mathbf{u}^{(k)})$, $\partial_i K^{(k)}(\mathbf{u}^{(k)})$, $E_r^t(u_i)$.

3 The General Form of Free Energy and Dissipation Functionals

We now construct (2.7) for the nonlinear material under consideration.

3.1 Free Energies

For a scalar theory the form of a free energy is given by

$$\psi(t) = \phi(t) + \sum_{k=1}^{N} \psi_{2k}(t),$$

$$\psi_{2k}(t) = \frac{1}{2k} \int_0^\infty \widetilde{G}^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}^t(u_i) d\mathbf{u}^{(2k)} \tag{3.1}$$

$$= \frac{1}{2k} \int_0^\infty \mathcal{G}^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r^t(u_i) d\mathbf{u}^{(2k)}.$$

The quantity $\phi(t)$ is the static limit of $\psi(t)$. The multiplying constants are chosen so the they lead to a constant equal to unity on the stress functionals introduced below. Using $(3.1)_2$, we see that

$$\psi_{2k}(t) = -\phi_e^{(2k)}(t) + \frac{1}{2k} \int_0^\infty G^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}^t(u_i) d\mathbf{u}^{(2k)},$$

$$\phi_e^{(2k)}(t) = \frac{1}{2k} G_\infty^{(2k)} [E(t)]^{2k}. \tag{3.2}$$

Note that the kernel $G^{(2k)}$ has been used here instead of $\widetilde{G}^{(2k)}$. A simple choice for $\phi(t)$ in $(3.1)_1$ is given by

$$\phi(t) = \sum_{k=1}^{N} \phi^{(2k)}(t),$$

$$\phi^{(2k)}(t) = \frac{1}{2k} G_\infty^{(2k)} [E(t)]^{2k}, \tag{3.3}$$

and we have

$$\psi(t) = \sum_{k=1}^{N} \psi_{2k}^{(0)}(t),$$

$$\psi_{2k}^{(0)}(t) = \frac{1}{2k} \int_0^\infty G^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}^t(u_i) d\mathbf{u}^{(2k)}. \tag{3.4}$$

Another version of these formulae, obtained by a change of variables, is given by

$$\psi_{2k}(t) = \frac{1}{2k} \int_{-\infty}^{t} \widetilde{G}^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}(u_i) d\mathbf{u}^{(2k)}$$

$$= \frac{1}{2k} \int_{-\infty}^{t} \mathcal{G}^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r(u_i) d\mathbf{u}^{(2k)}, \tag{3.5}$$

where $\mathbf{t}^{(n)} = (t, t, \ldots, t) \in (\mathbb{R})^n$.

Observe, from for example $(3.1)_3$, that ψ_{2k} is a polynomial of order $2k$ in $E(t)$. Also, $\psi(t) = \tilde{\psi}(E_r^t, E(t))$ is a polynomial of order $2N$ in $E(t)$, while the stress function $T(t) = \tilde{T}(E_r^t, E(t))$, introduced below, is a polynomial of order $2N - 1$. Examples of these polynomials are given below.

There is a further form for a free energy functional:

$$\psi(t) = S(t) + \sum_{k=1}^{N} \psi_{2k}^{(1)}(t),$$

$$\psi_{2k}^{(1)}(t) = \frac{1}{2k} \int_0^\infty \mathcal{G}^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E^t(u_i) d\mathbf{u}^{(2k)},$$

where

$$
\begin{aligned}
S(t) &= \int_0^{E(t)} \tilde{T}(E^t, E') dE' \\
&= E(t)T(t) - \int_0^{E(t)} E' \frac{\partial}{\partial E'} \tilde{T}(E^t, E') dE' \\
&= E(t)T(t) - \frac{1}{2} E^2(t) \frac{\partial}{\partial E(t)} T(t) + \frac{1}{2} \int_0^{E(t)} (E')^2 \frac{\partial^2}{\partial E'^2} \tilde{T}(E^t, E') dE' \\
&= E(t)T(t) - \frac{1}{2} E^2(t) \frac{\partial}{\partial E(t)} T(t) + \frac{1}{6} E^3(t) \frac{\partial^2}{\partial E(t)^2} T(t) \\
&\quad - \frac{1}{6} \int_0^{E(t)} (E')^3 \frac{\partial^3}{\partial E'^3} \tilde{T}(E^t, E') dE'.
\end{aligned}
$$

The first form given for the quantity $S(t)$ is required to ensure that (2.5) holds. The others result from repeated integrations by parts. The two general terms are

$$(-1)^{k-1} \left\{ \frac{1}{k!} E^k(t) \frac{\partial^{k-1}}{\partial E(t)^{k-1}} T(t) - \frac{1}{k!} \int_0^{E(t)} (E')^k \frac{\partial^k}{\partial E'^k} \tilde{T}(E^t, E') dE' \right\},$$

$$k = 1, 2, \dots.$$

As noted above, all quantities of interest, in the present model, are polynomials in $E(t)$ of order $2N$ or lower, in particular, the stress function $T(t)$, which is a polynomial of order $2N - 1$. In this context, we refer to (4.2). Thus, if $k = 2N$, the integral and all subsequent terms in (3.8) vanish.

3.2 Dissipation Functionals

The rate of dissipation has the form

$$D(t) = \sum_{k=1}^{N} D_{2k}(t),$$

$$D_{2k}(t) = -\frac{1}{2k} \int_0^\infty K^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}^t(u_i) d\mathbf{u}^{(2k)}$$

$$= -\frac{1}{2k} \int_0^\infty \mathcal{K}^{(2k)}(\mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r^t(u_i) d\mathbf{u}^{(2k)} \tag{3.9}$$

$$= -\frac{1}{2k} \int_{-\infty}^t K^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} \dot{E}(u_i) d\mathbf{u}^{(2k)}$$

$$= -\frac{1}{2k} \int_{-\infty}^t \mathcal{K}^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r(u_i) d\mathbf{u}^{(2k)}.$$

A question which immediately arises is what choices of the functions $K^{(2k)}(\mathbf{u}^{(2k)})$ ensures that $D(t)$ will be nonnegative? The simplest choice is to assume that $K^{(2k)}$ is completely factorizable, giving

$$K^{(2k)}(\mathbf{u}^{(2k)}) = \prod_{i=1}^{2k} d_k(u_i), \tag{3.10}$$

so that

$$D_{2k}(t) = [B_{2k}(t)]^{2k} \geq 0,$$
$$B_{2k}(t) = \int_0^\infty d_{2k}(u) \dot{E}^t(u) du. \tag{3.11}$$

This option is discussed further in Sect. 6.

3.3 Non-uniqueness of the Free Energy

The kernels $G^{(2k)}(\mathbf{u}^{(2k)})$ and $\mathcal{G}^{(2k)}(\mathbf{u}^{(2k)})$ are not uniquely given. If we add a term $G_1^{(2k)}(\mathbf{u}^{(2k)})$ to $G^{(2k)}(\mathbf{u}^{(2k)})$, such that the positivity requirements are preserved but $G_1^{(2k)}(\mathbf{u}^{(2k)})$ has the property

$$G_1^{(2k)}(\mathbf{u}^{(2k-1)}, 0) = 0, \tag{3.12}$$

then the functional (3.1) remains a valid free energy, yielding the same stress function. Such a change effects $K^{(2k)}(\mathbf{u}^{(2k)})$ and $\mathcal{K}^{(2k)}(\mathbf{u}^{(2k)})$ also. This line of argument suggests that there are typically many free energies and dissipation functionals corresponding to a given constitutive relation for stress. Such properties are known to exist for the linear model (see for example [8]). Discussion of this issue and how to achieve uniqueness may be found in [9].

3.4 The Stress Function

Let $T(t)$ be the stress at time t, determined by (2.5). Then the constitutive relation has the equivalent forms

$$T(t) = T_e(t) + \sum_{k=1}^N T_{2k-1}(t),$$

$$T_1(t) = \int_0^\infty \mathcal{G}^{(1)}(u_1) E_r^t(u_1) du_1 = \int_0^\infty \widetilde{G}^{(1)}(u_1) \dot{E}^t(u_1) du_1,$$

$$T_3(t) = \int_0^\infty \mathcal{G}^{(3)}(u_1, u_2, u_3) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) du_1 du_2 du_3$$

$$= \int_0^\infty \widetilde{G}^{(3)}(u_1, u_2, u_3) \dot{E}^t(u_1) \dot{E}^t(u_2) \dot{E}^t(u_3) du_1 du_2 du_3, \tag{3.13}$$

$$T_{2k-1}(t) = \int_0^\infty \mathcal{G}^{(2k-1)}(\mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k-1} E_r^t(u_i) d\mathbf{u}^{(2k-1)}$$

$$= \int_0^\infty \widetilde{G}^{(2k-1)}(\mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k-1} \dot{E}^t(u_i) d\mathbf{u}^{(2k-1)}.$$

An alternative form is

$$T_{2k-1}(t) = \int_{-\infty}^t \mathcal{G}^{(2k-1)}(\mathbf{t}^{(2k-1)} - \mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k-1} E_r(u_i) d\mathbf{u}^{(2k-1)}$$

$$= \int_{-\infty}^t \widetilde{G}^{(2k-1)}(\mathbf{t}^{(2k-1)} - \mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k-1} \dot{E}(u_i) d\mathbf{u}^{(2k-1)}. \tag{3.14}$$

The quantity $T_e(t)$ is the stress function for the equilibrium limit ($E_r^t(u) = 0$, $u \in \mathbb{R}^+$) and the quantity $G^{(1)}(\cdot): \mathbb{R}^+ \mapsto \mathbb{R}^+$ is the linear relaxation function of the material. The quantity $T_e(t)$ in (2.4) is given by

$$T_e(t) = \frac{\partial \phi(t)}{\partial E(t)}. \tag{3.15}$$

For odd choices of k, the quantities $G^{(k)}(\mathbf{u}^{(k)})$, $\mathcal{G}^{(k)}(\mathbf{u}^{(k)})$, $k = 1, 3, \ldots, 2N - 1$ are assumed to be nonnegative, as is true for $k = 1$.

Remark 3.1 Condition (2.5) is satisfied provided that

$$G^{(2k-1)}(\mathbf{u}^{(2k-1)}) = G^{(2k)}(\mathbf{u}^{(2k-1)}, 0), \quad k = 1, 2, \ldots, N, \tag{3.16}$$

where $G^{(2k-1)}(\mathbf{u}^{(2k-1)})$ is the kernel in the stress function (see (3.13)) corresponding to $G^{(2k)}(\mathbf{u}^{(2k)})$. Any kernel with $2k - 1$ parameters could be indicated by $G^{(2k-1)}(\mathbf{u}^{(2k-1)})$, but we choose to reserve this notation for those occurring in the definition of stress, obeying (3.16). An alternative form of (3.16) is given by

$$\mathcal{G}^{(2k-1)}(\mathbf{u}^{(2k-1)}) = \prod_{i=1}^{2k-1} \partial_i G^{(2k)}(\mathbf{u}^{(2k-1)}, 0), \quad k = 1, 2, \ldots, N. \tag{3.17}$$

The assertion in (3.17) may be demonstrated with the aid of (2.2), (3.1)$_3$ and (3.14)$_1$.

Remark 3.2 The kernels $G^{(2k-1)}(\mathbf{u}^{(2k-1)})$ are assumed to be determined by the material under consideration. In other words, we can determine the kernel by a series of measurements of the stress function, for given strain histories ([10], Chap. 5, Sect. 2). This means that the stress function $\tilde{T}(E^t, E(t))$ and indeed the quantity $S(t)$, given by (3.7), are uniquely associated with the material. The non-uniqueness associated with $\psi(t)$ lies in the term after $S(t)$ in (3.6).

3.5 Symmetry Under Sign Inversion

We have

$$\psi(t) = \tilde{\psi}(E_r^t, E(t)) = \tilde{\psi}(-E_r^t, -E(t)),$$

$$D(t) = \tilde{D}((E^t, E(t)) = \tilde{D}(-E^t, -E(t)), \qquad (3.18)$$

$$\mathcal{D}(t) = \tilde{\mathcal{D}}((E^t, E(t)) = \tilde{\mathcal{D}}(-E^t, -E(t)).$$

The stress function derivable from a free energy, in accordance with (2.5), only has odd powers of the stress history, so it has the property that

$$T(t) = \tilde{T}(E^t, E(t)) = -\tilde{T}(-E^t, -E(t)). \qquad (3.19)$$

3.6 The Work Function

Basic properties of $W(t)$ are

$$\dot{W}(t) = T(t)\dot{E}(t), \qquad \lim_{u \to -\infty} W(u) = 0. \qquad (3.20)$$

Let $\mathbf{uc}^{(2k-1)} = (u_{2k}, u_{2k}, \ldots, u_{2k}) \in (\mathbb{R}^+)^{2k-1}$. Explicit forms of $W(t)$ can be expressed as follows:

$$W(t) = \phi(t) + \sum_{k=1}^{N} W_{2k}(t),$$

$$W_{2k}(t) = \int_{-\infty}^{t} du_{2k} \int_{-\infty}^{u_{2k}} \widetilde{G}^{(2k-1)}(\mathbf{uc}^{(2k-1)} - \mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k} \dot{E}(u_i) d\mathbf{u}^{(2k-1)}. \qquad (3.21)$$

The second integral sign in $(3.21)_2$ indicates the presence of $2k - 1$ identical integral signs.

3.7 The Energy Equation

Let us now show that the energy conservation equation (2.7) holds, as a consequence of the above formulae. We use the second form of (3.5) for the free energy. The time derivative acting on the upper limit of the integrals give zero since $E_r(t) = 0$. The time derivative acting on the arguments $t - u_i$ can be replaced by $-\partial_i$, while if it is acting on $E_r(u_{2k})$, we obtain $-\dot{E}(t)$. In this term, the integral and derivative with respect to the selected variable u_{2k} cancel out to give u_{2k} a value t so that $t - u_{2k} = 0$. Thus,

$$\frac{d}{dt}\psi_{2k}(t) = \frac{1}{2k} \sum_{i=1}^{2k} \int_{-\infty}^{t} \partial_i \mathcal{G}^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r(u_i) d\mathbf{u}^{(2k)}$$

$$+ \dot{E}(t) \left[\int_{-\infty}^{t} \prod_{j=1}^{2k-1} \partial_j G^{(2k)}(\mathbf{t}^{(2k-1)} - \mathbf{u}^{(2k-1)}, 0) \prod_{i=1}^{2k-1} E_r(u_i) d\mathbf{u}^{(2k-1)} \right] \qquad (3.22)$$

$$= \frac{1}{2k} \int_{-\infty}^{t} \mathcal{K}^{(2k)}(\mathbf{t}^{(2k)} - \mathbf{u}^{(2k)}) \prod_{i=1}^{2k} E_r(u_i) d\mathbf{u}^{(2k)}$$

$$+ \dot{E}(t) \left[\int_{-\infty}^{t} \mathcal{G}^{(2k-1)}(\mathbf{t}^{(2k-1)} - \mathbf{u}^{(2k-1)}) \prod_{i=1}^{2k-1} E_r(u_i) d\mathbf{u}^{(2k-1)} \right].$$

The total symmetry between the arguments has been invoked. Using the last relation of (2.26), together with (3.9) and (3.14), we see that (3.22) implies (2.7).

4 Formulae for N=2

We now give the explicit version of a free energy, the corresponding rate of dissipation, together with the work and stress functions, all for $N = 2$.

The following identities make explicit the property referred to above, that all quantities of interest are polynomials in $E(t)$. In the quadratic case,

$$E_r^t(u_1) E_r^t(u_2) = E^t(u_1) E^t(u_2) - E(t) \left[E^t(u_1) + E^t(u_2) \right] + E^2(t), \qquad (4.1)$$

while for the quartic terms,

$$
\begin{aligned}
E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) E_r^t(u_4) = {} & E^t(u_1) E^t(u_2) E^t(u_3) E^t(u_4) \\
& - E(t) \big[E^t(u_1) E^t(u_2) E^t(u_3) + E^t(u_1) E^t(u_2) E^t(u_4) \\
& + E^t(u_1) E^t(u_3) E^t(u_4) + E^t(u_2) E^t(u_3) E^t(u_4) \big] \\
& + E^2(t) \big[E^t(u_1) E^t(u_2) + E^t(u_1) E^t(u_3) + E^t(u_2) E^t(u_3) \\
& + E^t(u_1) E^t(u_4) + E^t(u_2) E^t(u_4) + E^t(u_3) E^t(u_4) \big] \\
& - E^3(t) \big[E^t(u_1) + E^t(u_2) + E^t(u_3) + E^t(u_4) \big] + E^4(t).
\end{aligned}
\qquad (4.2)
$$

The form of a free energy is

$$
\begin{aligned}
\psi(t) = {} & \phi(t) + \frac{1}{2} \int_0^\infty \widetilde{G}^{(2)}(u_1, u_2) \dot{E}^t(u_1) \dot{E}^t(u_2) du_1 du_2 \\
& + \frac{1}{4} \int_0^\infty \widetilde{G}^{(4)}(u_1, u_2, u_3, u_4) \dot{E}^t(u_1) \dot{E}^t(u_2) \dot{E}^t(u_3). \\
& \qquad\qquad . \dot{E}^t(u_4) du_1 du_2 du_3 du_4 \\
= {} & \phi(t) + \frac{1}{2} \int_0^\infty \mathcal{G}^{(2)}(u_1, u_2) E_r^t(u_1) E_r^t(u_2) du_1 du_2 \\
& + \frac{1}{4} \int_0^\infty \mathcal{G}^{(4)}(u_1, u_2, u_3, u_4) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3). \\
& \qquad\qquad . E_r^t(u_4) du_1 du_2 du_3 du_4,
\end{aligned}
\qquad (4.3)
$$

or

$$\psi(t) = \phi(t) + \frac{1}{2}\int_{-\infty}^{t} \widetilde{G}^{(2)}(t-u_1, t-u_2)\dot{E}(u_1)\dot{E}(u_2)du_1du_2$$

$$+ \frac{1}{4}\int_{-\infty}^{t} \widetilde{G}^{(4)}(t-u_1, t-u_2, t-u_3, t-u_4).$$

$$.\dot{E}(u_1)\dot{E}(u_2)\dot{E}(u_3)\dot{E}(u_4)du_1du_2du_3du_4$$

$$= \phi(t) + \frac{1}{2}\int_{-\infty}^{t} \mathcal{G}^{(2)}(t-u_1, t-u_2)E_r(u_1)E_r(u_2)du_1du_2$$

$$+ \frac{1}{4}\int_{-\infty}^{t} \mathcal{G}^{(4)}(t-u_1, t-u_2, t-u_3, t-u_4).$$

$$.E_r(u_1)E_r(u_2)E_r(u_3)E_r(u_4)du_1du_2du_3du_4. \tag{4.4}$$

Relation (3.7) becomes in this context

$$S(t) = E(t)T(t) - \frac{1}{2}E^2(t)\frac{\partial}{\partial E(t)}T(t) + \frac{1}{6}E^3(t)\frac{\partial^2}{\partial E(t)^2}T(t)$$

$$- \frac{1}{24}E^4(t)\frac{\partial^3}{\partial E(t)^3}T(t). \tag{4.5}$$

Alternatively, using (4.1) and (4.2), together with symmetry properties, relation (4.3) takes the form

$$\psi(t) = S(t) + \frac{1}{2}\int_0^{\infty} \mathcal{G}^{(2)}(u_1, u_2)E^t(u_1)E^t(u_2)du_1du_2$$

$$+ \frac{1}{4}\int_0^{\infty} \mathcal{G}^{(4)}(u_1, u_2, u_3, u_4).$$

$$.E^t(u_1)E^t(u_2)E^t(u_3)E^t(u_4)du_1du_2du_3du_4,$$

$$S(t) = \phi_0(t) + \int_0^{\infty} \mathcal{G}_2^{(1)}(u_1)E^t(u_1)du_1 E(t)$$

$$+ \int_0^{\infty} \mathcal{G}^{(3)}(u_1, u_2, u_3)E^t(u_1)E^t(u_2)E^t(u_3)du_1du_2du_3 E(t)$$

$$+ \frac{3}{2}\int_0^{\infty} \mathcal{G}_4^{(2)}(u_1, u_2)E^t(u_1)E^t(u_2)du_1du_2 E^2(t),$$

$$+ \int_0^{\infty} \mathcal{G}_4^{(1)}(u_1)E^t(u_1)du_1 E^3(t), \tag{4.6}$$

where

$$\phi_0(t) = \frac{1}{2}G^{(2)}(0)E^2(t) + \frac{1}{4}G^{(4)}(0)E^4(t),$$

$$\mathcal{G}_2^{(1)}(u_1) = \partial_1 G^{(2)}(u_1, 0), \quad G^{(2)}(0) = G^{(2)}(0, 0),$$

$$\mathcal{G}^{(3)}(u_1, u_2, u_3) = \partial_1\partial_2\partial_3 G^{(4)}(u_1, u_2, u_3, 0), \tag{4.7}$$

$$\mathcal{G}_4^{(2)}(u_1, u_2) = \partial_1 \partial_2 G^{(4)}(u_1, u_2, 0, 0),$$

$$\mathcal{G}_4^{(1)}(u_1) = \partial_1 G^{(4)}(u_1, 0, 0, 0), \quad G^{(4)}(0) = G^{(4)}(0, 0, 0, 0).$$

Note that $(4.7)_{2,4}$ are examples of (3.16).

We can write $S(t)$ as a polynomial in $E(t)$, as follows

$$S(t) = S_1 E(t) + S_2 E^2(t) + S_3 E^3(t) + S_4 E^4(t),$$

$$S_1 = \int_0^\infty \mathcal{G}_2^{(1)}(u_1) E^t(u_1) du_1$$

$$+ \int_0^\infty \mathcal{G}^{(3)}(u_1, u_2, u_3) E^t(u_1) E^t(u_2) E^t(u_3) du_1 du_2 du_3,$$

$$S_2 = \frac{3}{2} \int_0^\infty \mathcal{G}_4^{(2)}(u_1, u_2) E^t(u_1) E^t(u_2) du_1 du_2 + + \frac{1}{2} G^{(2)}(0), \tag{4.8}$$

$$S_3 = \int_0^\infty \mathcal{G}_4^{(1)}(u_1) E^t(u_1) du_1,$$

$$S_4 = \frac{1}{4} G^{(4)}(0).$$

For $N = 1$, the case where the stress function is a linear history of the strain, $S(t)$ takes the form

$$S(t) = E(t)T(t) - \frac{1}{2} G^{(2)}(0) E^2(t), \tag{4.9}$$

which is familiar in various contexts [1].

The stress function is given by

$$T(t) = T_e(t) + \int_0^\infty \widetilde{G}_2^{(1)}(u_1) \dot{E}^t(u_1) du_1$$

$$+ \int_0^\infty \widetilde{G}^{(3)}(u_1, u_2, u_3) \dot{E}^t(u_1) \dot{E}^t(u_2) \dot{E}^t(u_3)) du_1 du_2 du_3$$

$$= T_e(t) + \int_0^\infty \mathcal{G}_2^{(1)}(u_1) E_r^t(u_1) du_1 \tag{4.10}$$

$$+ \int_0^\infty \mathcal{G}^{(3)}(u_1, u_2, u_3) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) du_1 du_2 du_3,$$

$$T_e(t) = G_\infty^{(2)} E(t) + G_\infty^{(4)} E^3(t),$$

where $G_\infty^{(2)}$ and $G_\infty^{(4)}$ are special cases of the quantity introduced in (2.21). We have $\widetilde{G}_2^{(1)}(u_1) = G_2^{(1)}(u_1) - G_\infty^{(1)}$ where $G_2^{(1)}(u_1)$ is the linear relaxation function, while $\mathcal{G}_2^{(1)}(u_1)$ is the derivative of this linear relaxation function. Also, $\widetilde{G}^{(3)}(u_1, u_2, u_3) = G^{(3)}(u_1, u_2, u_3) - G_\infty^{(3)}$, the quantity $G^{(3)}(u_1, u_2, u_3)$ being a generalization of the linear relaxation in the context of cubic terms. The definitions of $\mathcal{G}_2^{(1)}(u_1)$ and $\mathcal{G}^{(3)}(u_1, u_2, u_3)$ in terms of more basic quantities are given in (4.7).

Alternatively, we can write the stress function as

$$
\begin{aligned}
T(t) &= T_e(t) + \int_{-\infty}^{t} \widetilde{G}_2^{(1)}(t - u_1)\dot{E}(u_1)du_1 \\
&\quad + \int_{-\infty}^{t} \widetilde{G}^{(3)}(t - u_1, t - u_2, t - u_3)\dot{E}(u_1)\dot{E}(u_2)\dot{E}(u_3))du_1 du_2 du_3 \\
&= T_e(t) + \int_{-\infty}^{t} \mathcal{G}_2^{(1)}(t - u_1)E_r(u_1)du_1 \\
&\quad + \int_{-\infty}^{t} \mathcal{G}^{(3)}(t - u_1, t - u_2, t - u_3)E_r(u_1)E_r(u_2)E_r(u_3)du_1 du_2 du_3.
\end{aligned}
\tag{4.11}
$$

Using $(4.10)_2$, the stress function can be written as a polynomial in $E(t)$:

$$
\begin{aligned}
T(t) &= T_0 + T_1 E(t) + T_2 E^2(t) + T_3 E^3(t), \\
T_0 &= \int_0^{\infty} \mathcal{G}_2^{(1)}(u_1)E^t(u_1)du_1 \\
&\quad + \int_0^{\infty} \mathcal{G}^{(3)}(u_1, u_2, u_3)E^t(u_1)E^t(u_2)E^t(u_3)du_1 du_2 du_3, \\
T_1 &= G^{(2)}(0) + 3\int_0^{\infty} \mathcal{G}_4^{(2)}(u_1, u_2)E^t(u_1)E^t(u_2)du_1 du_2, \\
T_2 &= 3\int_0^{\infty} \mathcal{G}_4^{(1)}(u_1)E^t(u_1)du_1, \\
T_3 &= G^{(4)}(0).
\end{aligned}
\tag{4.12}
$$

Substituting $(4.12)_1$ into (4.5), we obtain

$$
S(t) = T_0 E(t) + \frac{1}{2}T_1 E^2(t) + \frac{1}{3}T_2 E^3(t) + \frac{1}{4}T_3 E^4(t), \tag{4.13}
$$

or

$$
S_1 = T_0, \quad S_2 = \frac{1}{2}T_1, \quad S_3 = \frac{1}{3}T_2, \quad S_4 = \frac{1}{4}T_3. \tag{4.14}
$$

These relations could also be derived from (4.8) and (4.12).

The rate of dissipation will now be considered. From (2.26), we see that

$$
\begin{aligned}
K^{(2)}(u_1, u_2) &= \left\{ \frac{\partial}{\partial u_1} + \frac{\partial}{\partial u_2} \right\} G^{(2)}(u_1, u_2), \\
K^{(4)}(u_1, u_2, u_3, u_4) &= \left\{ \frac{\partial}{\partial u_1} + \frac{\partial}{\partial u_2} + \frac{\partial}{\partial u_3} + \frac{\partial}{\partial u_4} \right\} G^{(4)}(u_1, u_2, u_3, u_4).
\end{aligned}
\tag{4.15}
$$

Inverses of these relations are given by the following special cases of (2.29)

$$
\begin{aligned}
\widetilde{G}^{(2)}(u_1, u_2) &= -\int_0^{\infty} K^{(2)}(u_1 + z, u_2 + z)dz, \\
\widetilde{G}^{(4)}(u_1, u_2, u_3, u_4) &= -\int_0^{\infty} K^{(4)}(u_1 + z, u_2 + z, u_3 + z, u_4 + z)dz.
\end{aligned}
\tag{4.16}
$$

Equations $(4.15)_1$ and $(4.16)_1$ are familiar from the linear model [1, 7]. Similar relations to (4.15) and (4.16) are true for $\mathcal{K}^{(2)}$, $\mathcal{K}^{(4)}$ and $\mathcal{G}^{(2)}$, $\mathcal{G}^{(4)}$.

The rate of dissipation is given by

$$
\begin{aligned}
D(t) = &-\frac{1}{2}\int_0^\infty K^{(2)}(u_1, u_2)\dot{E}^t(u_1)\dot{E}^t(u_2)du_1du_2 \\
&-\frac{1}{4}\int_0^\infty K^{(4)}(u_1, u_2, u_3, u_4). \\
&\qquad .\dot{E}^t(u_1)\dot{E}^t(u_2)\dot{E}^t(u_23)\dot{E}^t(u_4)du_1du_2du_3du_4 \\
= &-\frac{1}{2}\int_0^\infty \mathcal{K}^{(2)}(u_1, u_2)E_r^t(u_1)E_r^t(u_2)du_1du_2 \\
&-\frac{1}{4}\int_0^\infty \mathcal{K}^{(4)}(u_1, u_2, u_3, u_4). \\
&\qquad .E_r^t(u_1)E_r^t(u_2)E_r^t(u_3)E_r^t(u_4)du_1du_2du_3du_4,
\end{aligned}
\tag{4.17}
$$

or

$$
\begin{aligned}
D(t) = &-\frac{1}{2}\int_{-\infty}^t K^{(2)}(t-u_1, t-u_2)\dot{E}(u_1)\dot{E}(u_2)du_1du_2 \\
&-\frac{1}{4}\int_{-\infty}^t K^{(4)}(t-u_1, t-u_2, t-u_3, t-u_4). \\
&\qquad .\dot{E}(u_1)\dot{E}(u_2)\dot{E}(u_3)\dot{E}(u_4)du_1du_2du_3du_4 \\
= &-\frac{1}{2}\int_{-\infty}^t \mathcal{K}^{(2)}(t-u_1, t-u_2)E_r(u_1)E_r(u_2)du_1du_2 \\
&-\frac{1}{4}\int_{-\infty}^t \mathcal{K}^{(4)}(t-u_1, t-u_2, t-u_3, t-u_4). \\
&\qquad .E_r(u_1)E_r(u_2)E_r(u_3)E_r(u_4)du_1du_2du_3du_4.
\end{aligned}
\tag{4.18}
$$

For $N = 2$, the expression (3.21) for the work function can be written as

$$
\begin{aligned}
W(t) = &\phi(t) + \int_{-\infty}^t du \int_{-\infty}^u du_1 G_2^{(1)}(u-u_1)\dot{E}(u)\dot{E}(u_1) \\
&+ \int_{-\infty}^t du \int_{-\infty}^u du_1 \int_{-\infty}^u du_2 \int_{-\infty}^u du_3 G^{(3)}(u-u_1, u-u_2, u-u_3). \\
&\qquad .\dot{E}(u)\dot{E}(u_1)\dot{E}(u_2)\dot{E}(u_3) \\
= &\phi(t) + \int_0^\infty du \int_u^\infty du_1 G_2^{(1)}(u-u_1)\dot{E}^t(u)\dot{E}^u(u_1) \\
&+ \int_0^\infty du \int_u^\infty du_1 \int_u^\infty du_2 \int_u^\infty du_3 G^{(3)}(u-u_1, u-u_2, u-u_3). \\
&\qquad .\dot{E}^t(u)\dot{E}^u(u_1)\dot{E}^u(u_2)\dot{E}^u(u_3)
\end{aligned}
\tag{4.19}
$$

$$= \phi(t) + \int_{-\infty}^{t} du \int_{-\infty}^{u} du_1 \mathcal{G}_2^{(1)}(u - u_1)(E(u) - E(t))(E(u_1) - E(u))$$

$$+ \int_{-\infty}^{t} du \int_{-\infty}^{u} du_1 \int_{-\infty}^{u} du_2 \int_{-\infty}^{u} du_3 \mathcal{G}^{(3)}(u - u_1, u - u_2, u - u_3).$$

$$.(E(u) - E(t))(E(u_1) - E(u))(E(u_2) - E(u))(E(u_3) - E(u))$$

$$= \phi(t) + \int_{0}^{\infty} du \int_{u}^{\infty} du_1 \mathcal{G}_2^{(1)}(u - u_1) E_r^t(u) E_r^u(u_1)$$

$$+ \int_{0}^{\infty} du \int_{u}^{\infty} du_1 \int_{u}^{\infty} du_2 \int_{u}^{\infty} du_3 \mathcal{G}^{(3)}(u - u_1, u - u_2, u - u_3).$$

$$.E_r^t(u) E_r^u(u_1) E_r^u(u_2) E_r^u(u_3).$$

The quadratic term can be written as

$$\int_{-\infty}^{t} du \int_{-\infty}^{u} du_1 G_2^{(1)}(u - u_1) \dot{E}(u) \dot{E}(u_1)$$

$$= \int_{-\infty}^{t} du_1 \int_{u_1}^{t} du \, G_2^{(1)}(u - u_1) \dot{E}(u) \dot{E}(u_1)$$

$$= \int_{-\infty}^{t} du \int_{u}^{t} du_1 G_2^{(1)}(u_1 - u) \dot{E}(u) \dot{E}(u_1) \qquad (4.20)$$

$$= \frac{1}{2} \int_{-\infty}^{t} du \int_{-\infty}^{t} du_1 G_2^{(1)}(|u - u_1|) \dot{E}(u) \dot{E}(u_1).$$

The quantity $W(t)$ cannot be regarded as a free energy if the property discussed in [11] is taken into account. However, from (2.8), it follows that it must be greater than or equal to the maximum free energy associated with the material, an observation which follows from (2.8) for any free energy $\psi(t)$. Thus, we have in general the requirement that

$$\psi(t) \le W(t). \qquad (4.21)$$

5 Discrete-Spectrum Materials

We will give the relevant formulae for $N = 2$. Generalization to larger values of N is relatively straightforward. Repeating certain relations from (4.3), we find that

$$\psi(t) = \phi(t) + \psi_2(t) + \psi_4(t),$$

$$\phi(t) = \frac{1}{2} G_\infty^{(2)} [E(t)]^2 + \frac{1}{4} G_\infty^{(4)} [E(t)]^4,$$

$$\psi_2(t) = \frac{1}{2} \int_0^\infty \widetilde{G}^{(2)}(u_1, u_2) \dot{E}^t(u_1) \dot{E}^t(u_2) du_1 du_2$$

$$= \frac{1}{2} \int_0^\infty \mathcal{G}^{(2)}(u_1, u_2)) E_r^t(u_1) E_r^t(u_2) du_1 du_2,$$

$$\psi_4(t) = \frac{1}{4} \int_0^\infty \widetilde{G}^{(4)}(u_1, u_2, u_3, u_4) \dot{E}^t(u_1) \dot{E}^t(u_2) \dot{E}^t(u_3) \dot{E}^t(u_4) du_1 du_2 du_3 du_4 \tag{5.1}$$

$$= \frac{1}{4} \int_0^\infty \mathcal{G}^{(4)}(u_1, u_2, u_3, u_4) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) E_r^t(u_4) du_1 du_2 du_3 du_4,$$

$$\widetilde{G}^{(2)}(u_1, u_2) = \sum_{i,j=1}^n C_{ij}^{(2)} e^{-\alpha_i u_1 - \alpha_j u_2},$$

$$\mathcal{G}^{(2)}(u_1, u_2) = \sum_{i,j=1}^n \alpha_i \alpha_j C_{ij}^{(2)} e^{-\alpha_i u_1 - \alpha_j u_2},$$

$$\widetilde{G}^{(4)}(u_1, u_2, u_3, u_4) = \sum_{i,j,k,l=1}^n C_{ijkl}^{(4)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3 - \alpha_l u_4},$$

$$\mathcal{G}^{(4)}(u_1, u_2, u_3, u_4) = \sum_{i,j,k,l=1}^n \alpha_i \alpha_j \alpha_k \alpha_l C_{ijkl}^{(4)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3 - \alpha_l u_4},$$

where n is a positive integer and the inverse decay times α_i, $i = 1, 2, \ldots, n$, are positive. The quantities with components $C_{ij}^{(2)}$, $C_{ijkl}^{(4)}$ must be non-negative on $\mathbb{R}^n$, $\mathbb{R}^n \times \mathbb{R}^n$ respectively. This means that if λ_1, $i = 1, 2 \ldots, n$ are the components of a vector in $\mathbb{R}^n$ then

$$\sum_{ij=1}^n C_{ij}^{(2)} \lambda_i \lambda_j \geq 0, \qquad \sum_{ijkl=1}^n C_{ijkl}^{(4)} \lambda_i \lambda_j \lambda_k \lambda_l \geq 0, \tag{5.2}$$

for all choices of λ_i.

Remark 5.1 We are taking the values of the decay parameters α_j, $j = i, 2, \ldots, n$ and their total number n as equal for the quadratic and quartic terms, to avoid proliferation of subscripts and superscripts. In fact, we are free to choose them to be unequal, which can be indicated by assigning extra subscripts or superscripts to these parameters.

Also, from (4.17),

$$D(t) = D_2(t) + D_4(t),$$

$$D_2(t) = -\frac{1}{2} \int_0^\infty K^{(2)}(u_1, u_2) \dot{E}^t(u_1) \dot{E}^t(u_2) du_1 du_2$$

$$= -\frac{1}{2} \int_0^\infty \mathcal{K}^{(2)}(u_1, u_2)) E_r^t(u_1) E_r^t(u_2) du_1 du_2,$$

$$D_4(t) = -\frac{1}{4} \int_0^\infty K^{(4)}(u_1, u_2, u_3, u_4) \dot{E}^t(u_1) \dot{E}^t(u_2) \dot{E}^t(u_3) \dot{E}^t(u_4) du_1 du_2 du_3 du_4$$

$$= -\frac{1}{4} \int_0^\infty \mathcal{K}^{(4)}(u_1, u_2, u_3, u_4) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) E_r^t(u_4) du_1 du_2 du_3 du_4,$$

$$K^{(2)}(u_1, u_2) = -\sum_{i,j=1}^n \Gamma_{ij}^{(2)} e^{-\alpha_i u_1 - \alpha_j u_2}, \tag{5.3}$$

$$\mathcal{K}^{(2)}(u_1, u_2) = -\sum_{i,j=1}^{n} \alpha_i \alpha_j \Gamma_{ij}^{(2)} e^{-\alpha_i u_1 - \alpha_j u_2},$$

$$K^{(4)}(u_1, u_2, u_3, u_4) = -\sum_{i,j,k,l=1}^{n} \Gamma_{ijkl}^{(4)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3 - \alpha_l u_4},$$

$$\mathcal{K}^{(4)}(u_1, u_2, u_3, u_4) = -\sum_{i,j,k,l=1}^{n} \alpha_i \alpha_j \alpha_k \alpha_l \Gamma_{ijkl}^{(4)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3 - \alpha_l u_4},$$

$$\Gamma_{ij}^{(2)} = (\alpha_i + \alpha_j) C_{ij}^{(2)},$$

$$\Gamma_{ijkl}^{(4)} = (\alpha_i + \alpha_j + \alpha_k + \alpha_l) C_{ijkl}^{(4)},$$

where the summation convention is not in force. The matrices $\Gamma_{ij}^{(2)}$, $\Gamma_{ijkl}^{(4)}$ are independent of each other (note remark 5.1 in this context), so that, for example, one of them can be put equal to zero, if we wish to focus on the properties of the other.

These quantities $\Gamma_{ij}^{(2)}$, $\Gamma_{ijkl}^{(4)}$ are assumed to be non-negative in the sense of (5.2). This ensures that the second law $D(t) \geq 0$ is obeyed. Then, it follows from Proposition 2.1 that $C_{ij}^{(2)}$, $C_{ijkl}^{(4)}$ are also positive semi-definite quantities.

Using (4.7), (4.10) and (5.1), we see that the stress function is given by

$$T(t) = T_e(t) + T^{(1)}(t) + T^{(3)}(t),$$

$$T_e(t) = G_\infty^{(2)} E(t) + G_\infty^{(4)} [E(t)]^3,$$

$$T^{(1)}(t) = \int_0^\infty \mathcal{G}_2^{(1)}(u_1)) E_r^t(u_1) du_1,$$

$$T^{(3)}(t) = \int_0^\infty \mathcal{G}^{(3)}(u_1, u_2, u_3) E_r^t(u_1) E_r^t(u_2) E_r^t(u_3) du_1 du_2 du_3,$$

$$\mathcal{G}_2^{(1)}(u_1) = -\sum_{i=1}^{n} \alpha_i G_i^{(1)} e^{-\alpha_i u_1}$$

$$= -\sum_{i=1}^{n} \alpha_i \sum_{j=1}^{n} C_{ij}^{(2)} e^{-\alpha_i u_1}, \tag{5.4}$$

$$\mathcal{G}^{(3)}(u_1, u_2, u_3) = -\sum_{i,j,k=1}^{n} \alpha_i \alpha_j \alpha_k G_{ijk}^{(3)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3}$$

$$= -\sum_{i,j,k=1}^{n} \alpha_i \alpha_j \alpha_k \sum_{l=1}^{n} C_{ijkl}^{(4)} e^{-\alpha_i u_1 - \alpha_j u_2 - \alpha_k u_3}.$$

Thus, we must have

$$G_i^{(1)} = \sum_{j=1}^{n} C_{ij}^{(2)},$$

$$\tag{5.5}$$

$$G_{ijk}^{(3)} = \sum_{l=1}^{n} C_{ijkl}^{(4)},$$

where $G_i^{(1)}$, $i = 1, 2, \ldots, n$ are the coefficients of the exponentially decaying terms in the linear relaxation function and $G_{ijk}^{(3)}$, $i, j, k = 1, 2, \ldots, n$ are the corresponding quantities for the cubic nonlinear terms in the constitutive equations. The forms given in terms of $C_{ij}^{(2)}$ and $C_{ijkl}^{(4)}$ may be derived from (5.1), together with (4.7)$_{2,4}$. We note the points made after (4.10), in this context.

The vector $\mathbf{e}$ in $\mathbb{R}^n$ is defined by [1]

$$e_i(t) = -\alpha_i E_{r+}^t(-i\alpha_i) = E(t) - \alpha_i E_+^t(-i\alpha_i) = \frac{d}{dt} E_+^t(-i\alpha_i), \quad i = 1, 2, \ldots, n, \quad (5.6)$$

where

$$E_+^t(\omega) = \int_0^\infty E^t(s) e^{-i\omega s} ds. \quad (5.7)$$

The quantities $E_+^t(-i\alpha_i)$ are real. They are the Laplace transforms

$$E_+^t(-i\alpha_i) = \int_0^\infty E^t(s) e^{-\alpha_i s} ds. \quad (5.8)$$

We have

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

$$\frac{\partial}{\partial E(t)} e_i = 1, \quad i = 1, 2, \ldots, n. \quad (5.9)$$

Then,

$$\psi(t) = \phi(t) + \frac{1}{2} \sum_{ij=1}^n e_i C_{ij}^{(2)} e_j + \frac{1}{4} \sum_{ijkl=1}^n e_i e_j C_{ijkl}^{(4)} e_k e_l,$$

$$D(t) = \frac{1}{2} \sum_{ij=1}^n e_i \Gamma_{ij}^{(2)} e_j + \frac{1}{4} \sum_{ijkl=1}^n e_i e_j \Gamma_{ijkl}^{(4)} e_k e_l, \quad (5.10)$$

$$T(t) = T_e(t) + \sum_{ij=1}^n C_{ij}^{(2)} e_j + \sum_{ijkl=1}^n C_{ijkl}^{(4)} e_j e_k e_l.$$

6 Product Formulae for the Rate of Dissipation

Referring to (3.10), (2.29) and (2.27), we look at the case

$$K^{(2k)}(u_1, u_2, \ldots, u_{2k}) = -\prod_{l=1}^{2k} d_{2k}(u_l),$$

$$\mathcal{K}^{(2k)}(u_1, u_2, \ldots, u_{2k}) = -\prod_{l=1}^{2k} d_{2k}'(u_l),$$

$$\widetilde{G}^{(2k)}(u_1, u_2, \ldots, u_{2k}) = \int_0^\infty \prod_{l=1}^{2k} d_{2k}(u_l + z) dz, \quad (6.1)$$

$$\mathcal{G}^{(2k)}(u_1, u_2, \ldots, u_{2k}) = \int_0^\infty \prod_{l=1}^{2k} d'_{2k}(u_l + z)dz,$$

$$d'_{2k}(u) \to 0 \quad \text{as} \quad u \to \infty, \quad k = 1, 2, \ldots N.$$

Let

$$B_{2k}(t, z) = \int_0^\infty d_{2k}(u + z)\dot{E}^t(u)du = \int_z^\infty d_{2k}(s)\dot{E}^{t+z}(s)ds$$

$$= \int_0^\infty d'_{2k}(u + z)E_r^t(u)du = \int_z^\infty d'_{2k}(s)E_r^t(s - z)ds, \tag{6.2}$$

$$B_{2k}(t) = B_{2k}(t, 0).$$

Also,

$$F(t, z) = \sum_{k=1}^\infty a_{2k}[B_{2k}(t, z)]^{2k}, \qquad F(t) = F(t, 0), \tag{6.3}$$

where the coefficients a_r, $r = 2, 4, \ldots$ are assumed to be nonnegative quantities, so that the function $F(t, z)$ is also nonnegative. If the summations are infinite, we must assume convergence. The form $(6.2)_3$ will be used. Then,

$$D(t) = F(t), \qquad \psi(t) = \phi(t) + \int_0^\infty F(t, z)dz,$$

$$\mathcal{D}(t) = \int_{-\infty}^t F(s)ds = \int_0^\infty F(t - z)dz,$$

$$T(t) = \frac{\partial}{\partial E(t)}\psi(t) = T_e(t) + \int_0^\infty \frac{\partial}{\partial E(t)}F(t, z)dz, \tag{6.4}$$

$$\frac{\partial}{\partial E(t)}F(t, z) = \sum_{k=1}^\infty 2k a_{2k}[B_{2k}(t, z)]^{2k-1}(d_{2k}(z) - d_{2k}(\infty)).$$

The stress $T(t)$ emerges from $(6.4)_{5,6,7}$ and differentiating the term $E(t)$ in $E_r^t(u) = E(t - u) - E(t)$ with respect to $E(t)$.

Let us check that (2.7) holds. The contribution $T(t)\dot{E}(t)$ follows from $T(t)$ determined as above. The quantity $D(t)$ arises by differentiating $E^t(u) = E(t - u)$ with respect to t in $(6.2)_2$, treating $E(t)$ as a constant. This action will be denoted by ∂_d. Using the same manipulation as in (2.4), we see that

$$\int_0^\infty d'_{2k}(u + z)\frac{\partial}{\partial t}E^t(u)du = -\int_0^\infty d'_{2k}(u + z)\frac{\partial}{\partial u}E^t(u)du$$

$$= -\int_0^\infty d'_{2k}(u + z)\frac{\partial}{\partial u}E_r^t(u)du = \int_0^\infty d''_{2k}(u + z)E_r^t(u)du \tag{6.5}$$

$$= \int_0^\infty \frac{\partial}{\partial z}d'_{2k}(u + z)E_r^t(u)du.$$

Then,

$$
\begin{aligned}
\partial_d F(t, z) &= \sum_{k=1}^{\infty} 2k a_{2k} [B_{2k}(t, z)]^{2k-1} \int_0^{\infty} \frac{\partial}{\partial z} d'_{2k}(u+z) E_r^t(u) du \\
&= \frac{\partial}{\partial z} \left[\sum_{k=1}^{\infty} a_{2k} [B_{2k}(t, z)]^{2k} \right],
\end{aligned}
\tag{6.6}
$$

so that

$$
\partial_d \psi(t) = \int_0^{\infty} \partial_d F(t, z) dz = -F(t) = -D(t).
\tag{6.7}
$$

Remark 6.1 Observe that discrete spectrum materials, discussed in Sect. 5, are particular examples of (6.1) if the matrices Γ_{ij} and Γ_{ijkl} are factorizable in the sense that

$$
\Gamma_{ij} = \gamma_i^{(2)} \gamma_j^{(2)}, \qquad \Gamma_{ijkl} = \gamma_i^{(4)} \gamma_j^{(4)} \gamma_k^{(4)} \gamma_l^{(4)}, \qquad i, j, k, l = 1, 2, \ldots, n,
\tag{6.8}
$$

where $\gamma_i^{(2)}, \gamma_i^{(4)} \in \mathbb{R}^+$.

6.1 Exact Summations for a Simple Model

Let us now specialize further to the case where the functions d_{2k} are the same for all terms so that

$$
\begin{aligned}
K^{(2k)}(u_1, u_2, \ldots, u_{2k}) &= -\prod_{l=1}^{2k} d(u_l), \\
\mathcal{K}^{(2k)}(u_1, u_2, \ldots, u_{2k}) &= -\prod_{l=1}^{2k} d'(u_l), \\
\widetilde{G}^{(2k)}(u_1, u_2, \ldots, u_{2k}) &= \int_0^{\infty} \prod_{l=1}^{2k} d(u_l + z) dz, \\
\mathcal{G}^{(2k)}(u_1, u_2, \ldots, u_{2k}) &= \int_0^{\infty} \prod_{l=1}^{2k} d'(u_l + z) dz.
\end{aligned}
\tag{6.9}
$$

We put

$$
\begin{aligned}
B(t, z) &= \int_0^{\infty} d(u+z) \dot{E}^t(u) du = \int_z^{\infty} d(s) \dot{E}^t(s-z) ds \\
&= \int_0^{\infty} d'(u+z) E_r^t(u) du = \int_z^{\infty} d'(s) E_r^t(s-z) ds, \\
B(t) &= B(t, 0).
\end{aligned}
\tag{6.10}
$$

Also,

$$
F(t, z) = \sum_{k=1}^{\infty} a_{2k} [B(t, z)]^{2k}, \qquad F(t) = F(t, 0),
\tag{6.11}
$$

where the coefficients a_l, $l = 2, 4, 6 \ldots$ are assumed to be nonnegative quantities, so that the function $F(t, z)$ is also nonnegative. Then, the general forms of the rate of dissipation, free energy, total dissipation and stress function are given by the first six relations of (6.4). The general shape of $D(t)$ should be obtained from experiments. We make a mathematically convenient choice, taking

$$a_{2k} = \frac{(-1)^{k-1}C}{k!}, \quad k = 1, 2, \ldots, \tag{6.12}$$

which gives

$$F(t, z) = C[1 - e^{-B^2(t,z)}], \tag{6.13}$$

where C is a positive constant. This is zero for vanishing strain and C for large strain. Thus, using (6.4), we have

$$D(t) = C[1 - e^{-B^2(t)}], \qquad \psi(t) = \phi(t) + C \int_0^\infty [1 - e^{-B^2(t,z)}]dz,$$

$$\mathcal{D}(t)) = C \int_{-\infty}^t [1 - e^{-B^2(v)}]dv = C \int_0^\infty [1 - e^{-B^2(t-z)}]dz, \tag{6.14}$$

$$T(t) = \frac{\partial}{\partial E(t)} \psi(t) = T_e(t) + 2C \int_0^\infty (d(z) - d(\infty))B(t, z)e^{-B^2(t,z)}dz.$$

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