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ALGEBRAIC AND NUMERICAL EXPLORATION OF FREE ENERGIES FOR MATERIALS WITH MEMORY

GIOVAMBATTISTA AMENDOLA, MAURO FABRIZIO, JOHN MURROUGH GOLDEN

Abstract. We study the forms of a range of free energy functionals for materials with memory for two types of strain history, namely sinusoidal and exponential behaviours. The work deals with discrete spectrum materials, which are those with relaxation functions given by sums of decaying exponentials. Various standard free energy functionals are explored, including the minimum free energy and related quantities. It is shown that quite different formulae are obtained, depending on the manner in which these functionals are evaluated, particularly for those related to the minimum free energy. Such differences are resolved. Various numerical plots of free energies are presented and discussed, along with the rates of dissipation associated with them. This is the first comprehensive exploration of quantitative comparisons between the various free energy functionals. The results both illustrate certain properties that have been deduced theoretically and expose an interesting proximity between apparently unconnected functionals.

1. Introduction

Explicit algebraic representations of the minimum and related free energies have been given for materials with memory which have constitutive equations for stress given by linear functionals of the strain [16, 7, 11, 14, 12, 17, 18, 2] over the past fifteen years. We consider for definiteness here only isothermal mechanical problems, indeed those for solid viscoelastic materials. For simplicity (of presenting plots), only the scalar case is considered. It must be emphasized however that similar results can be given with little extra difficulty, at least in principle, for viscoelastic fluids, non-isothermal problems, electromagnetism, non-simple materials etc. as presented in the references noted above.

More classical examples of free energies were given and discussed in earlier references, notably the Graffi-Volterra and Dill functionals [19, 21, 6, 5]. There is also a new free energy functional introduced more recently [8] which is an explicit functional of the minimal state.

All discussion in these references has been in general algebraic terms, including proofs of various properties of the free energy functionals. The purpose of the present work is to present detailed algebraic and numerical representations of the

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various functionals noted above for particular examples of relaxation functions and strain histories, in order to discuss their properties and the relationships between them. It is shown that quite different formulae are obtained, depending on the manner in which these functionals are evaluated, particularly for those related to the minimum free energy. Such differences are resolved.

The discussion is confined to completely linear materials, namely those for which the expression for the stress is fully linear, including the portion that does not depend on memory, though in fact when developing the theoretical formulae, it is necessary to assume only linear memory terms; the portion not depending on memory may be non-linear.

A useful outcome of this work is to provide a compendium of completely explicit elementary scalar formulae relating to a range of functionals that are often discussed in the literature in very general terms.

2. A QUADRATIC MODEL FOR FREE ENERGIES

There are generally many free energies associated with a material with memory. They form a bounded convex set with a minimum and a maximum element ([10] for example). For a scalar theory with a linear constitutive relation for the stress, the most general form of a free energy is

$$\begin{gathered}\psi(t)=\phi(t)+\frac{1}{2}\int_0^\infty\int_0^\infty E_r^t(s)G_{12}(s,u)E_r^t(u)\,ds\,du,\\ G_{12}(s,u)=\frac{\partial^2}{\partial s\partial u}G(s,u),\quad \phi(t)=\frac{1}{2}G_\infty E^2(t),\\ G_\infty=G(\infty,u)=G(s,\infty),\quad \forall s,u\in\mathbb{R}^+,\end{gathered}\tag{2.1}$$

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

$$E^t(s)=E(t-s),\quad E_r^t(s)=E^t(s)-E(t).\tag{2.2}$$

The function G must be such that the integral term in (2.1) is non-negative, which is an expression of the very general requirement on free energies [3]

$$\psi(t)\geq\phi(t).\tag{2.3}$$

Under certain mild restrictions on this quantity (for example [18]), we can deduce the constitutive relations

$$T(t)=G_\infty E(t)+\int_0^\infty G'(u)E_r^t(u)du=G_0E(t)+\int_0^\infty G'(u)E^t(u)du,\tag{2.4}$$

where the relaxation function $G(u)$ is defined by

$$\begin{gathered}G(u)=G(0,u)=G(u,0),\quad G_0=G(0),\\ G(\infty)=G_\infty,\quad G'(\infty)=0\end{gathered}\tag{2.5}$$

and the prime indicates differentiation with respect to the argument.

The fundamental relationships

$$\dot\psi(t)+D(t)=T(t)\dot E(t),\quad D(t)\geq 0\tag{2.6}$$

express the first and second law of thermodynamics respectively. The quantity $D(t)$ is the rate of dissipation of energy associated with $\psi(t)$. Integrating (2.6) over

$(-\infty, t]$ yields that

$$\psi(t) + \mathcal{D}(t) = W(t), \quad \mathcal{D}(t) \geq 0, \tag{2.7}$$

where

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

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

Remark 2.1. As $\psi(t)$ increases in magnitude, it follows from (2.7) that $\mathcal{D}(t)$ decreases. From (2.6), a similar statement applies to $\dot{\psi}(t)$ and $D(t)$. However, while the magnitude of ψ is of immediate physical interest (in particular, given the existence of a minimum and a maximum free energy), this is not necessarily true in most cases for $\dot{\psi}(t)$. In contrast to $\mathcal{D}(t)$, we do not expect in general a clear physical interpretation of any ordering of the magnitude of $D(t)$.

However, there may be a close relationship between $\psi(t)$ and $\dot{\psi}(t)$, such as occurs for exponential histories. In this case, as we shall see below, $\dot{\psi}(t)$ is equal to $2\lambda\psi(t)$, where $\lambda > 0$. Thus, any ordering of free energies gives rise to a similar ordering in their derivatives and the reverse ordering in the associated rates of dissipation.

Remark 2.2. The quantities

$$R_\psi = \frac{\psi(t)}{W(t)}, \quad R_{\mathcal{D}} = \frac{\mathcal{D}(t)}{W(t)} \tag{2.9}$$

can be regarded as measures of the total energy storage and total dissipation in the material. They clearly obey the constraint $R_\psi + R_{\mathcal{D}} = 1$. Plots of R_ψ, in a particular context, are presented later (figure 21).

The rate of dissipation can be determined from (2.6) to be

$$D(t) = -\frac{1}{2}\int_0^\infty \int_0^\infty E_r^t(s)[G_{121}(s,u) + G_{122}(s,u)]E_r^t(u)\,ds\,du, \tag{2.10}$$

where, as for G_{12} in (2.1), the subscripts on G indicate differentiation with respect to the first or second argument. The quantity G must also have the property that the integral in (2.10) is non-positive.

A viscoelastic state is defined in general by the history and current value of strain $(E^t, E(t))$. The concept of a minimal state, defined in [11] and based on the the work of Noll [22] (see also [5, 6, 20, 7, 2]), can be expressed as follows: two viscoelastic states $(E_1^t, E_1(t))$, $(E_2^t, E_2(t))$ are equivalent or in the same equivalence class or minimal state if

$$E_1(t) = E_2(t), \quad \int_0^\infty G'(s+\tau)\left[E_1^t(s) - E_2^t(s)\right]ds = 0 \quad \forall \tau \geq 0. \tag{2.11}$$

A functional of $(E^t, E(t))$ which yields the same value for all members of the same minimal state will be referred to as a functional of the minimal state or as a minimal state variable. We can replace the histories E_1^t, E_2^t, E^t in these statements by the relative histories $E_{1r}^t, E_{2r}^t, E_r^t$.

Remark 2.3. A fundamental distinction between materials is that for some relaxation functions, namely those with only isolated singularities (in the frequency domain), the set of minimal states is non-singleton, while if some branch cuts are present in the relaxation function, the material has only singleton minimal states [8, 2].

We will deal only with the simplest case of isolated singularities in this work, namely discrete spectrum materials. These are characterized by relaxation functions which, in the frequency domain, consist of a series of isolated simple poles on the positive imaginary axis. In the time domain, such relaxation functions are given by sums of strictly decaying exponentials. The simplest case of non-isolated singularities is a continuous spectrum material [9, 2] for which the relaxation function is given by integrals of density functions multiplying strictly decaying exponentials.

The limit of discrete spectrum materials where the simple poles are more and more closely packed can be seen intuitively to be the continuous spectrum case. One feature of this transition will be explored in the present work, namely that noted in remark 3.1.

2.1. **Frequency domain quantities.**

Let Ω be the complex ω plane and

$$\begin{aligned} \Omega^{+} &= \{\omega \in \Omega : Im(\omega) \in \mathbb{R}^{+}\}, \\ W^{(+)} &= \{\omega \in \Omega : Im(\omega) \in \mathbb{R}^{++}\}. \end{aligned} \tag{2.12}$$

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

For any $f \in L^2(\mathbb{R})$, we denote its Fourier transform by

$$f_F(\omega) = \int_{-\infty}^{\infty} f(\xi) e^{-i\omega\xi} d\xi, \quad f_F \in L^2(\mathbb{R}). \tag{2.13}$$

It is often assumed in this context that $f \in L^1(\mathbb{R}) \cap L^2(\mathbb{R})$ or has equivalent properties on $\mathbb{R}^{\pm}$. If f is a real-valued function in the time domain - which will be the case for all functions of interest here - then

$$\overline{f_F}(\omega) = f_F(-\omega), \quad \omega \in \mathbb{R}, \tag{2.14}$$

where the bar denotes complex conjugate. We have

$$\begin{aligned} f_F(\omega) &= f_{+}(\omega) + f_{-}(\omega), \\ f_{+}(\omega) &= \int_{0}^{\infty} f(\xi) e^{-i\omega\xi} d\xi, \\ f_{-}(\omega) &= \int_{-\infty}^{0} f(\xi) e^{-i\omega\xi} d\xi, \quad f_{\pm} \in L^2(\mathbb{R}^{\pm}). \end{aligned} \tag{2.15}$$

The quantity f_{+} is analytic in Ω^{-}. For relevant functions in the present work, we also assume that it is analytic on an open set including $\mathbb{R}$ and thus on Ω^{-}. Similarly, f_{-} is analytic on Ω^{+}.

Functions on $\mathbb{R}$ which vanish identically on $\mathbb{R}^{--}$ are defined as functions on $\mathbb{R}^{+}$. For such quantities, $f_F = f_{+} = f_c - i f_s$ where f_c, f_s are the Fourier cosine and sine transforms

$$\begin{aligned} f_c(\omega) &= \int_{0}^{\infty} f(\xi) \cos\omega\xi d\xi = f_c(-\omega), \\ f_s(\omega) &= \int_{0}^{\infty} f(\xi) \sin\omega\xi d\xi = -f_s(-\omega). \end{aligned} \tag{2.16}$$

Thus,

$$G'_F(\omega) = G'_+(\omega) = \int_0^\infty G'(s)e^{-i\omega s}ds = G'_c(\omega) - iG'_s(\omega). \tag{2.17}$$

The property of G'_+ that

$$\lim_{\omega\to\infty} i\omega G'_+(\omega) = G'(0). \tag{2.18}$$

will be required. Properties of $G'_s(\omega)$ include

$$\begin{gathered} G'_s(\omega) \le 0 \quad \forall\omega \in \mathbb{R}^{++}, \\ G'_s(-\omega) = -G'_s(\omega), \quad \forall\omega \in \mathbb{R}, \end{gathered} \tag{2.19}$$

the first relation being a consequence of the second law of thermodynamics [10, 2] and the second being a particular case of $(2.16)_2$. It follows that $G'_s(0) = 0$. We also have [10, 2]

$$G_\infty - G_0 < 0, \quad G_\infty > 0, \tag{2.20}$$

the latter relation being true for a viscoelastic solid. The function $G'_+(\omega)$ is analytic on Ω^-, as indicated after (2.15). This implies that any singularities are at least slightly off the real axis into $W^{(+)}$, which in turn means that G' decays exponentially at large positive times, though perhaps weakly.

Because G' is real, we have from (2.17)

$$\overline{G'_+(\omega)} = G'_+(-\overline{\omega}). \tag{2.21}$$

This constraint in fact means that the singularities are symmetric under reflection in the positive imaginary axis. It generalizes the property expressed by (2.14).

The quantity $\overline{G'_+}(\omega)$ is analytic in Ω^+, its singularity structure being a mirror image, in the real axis, of that of $G'_+(\omega)$. Thus, $G'_s(\omega)$ has singularities in both $W^{(+)}$ and $W^{(-)}$ which are mirror images of one another. Similarly, its zeros will be mirror images of one another.

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

$$H(\omega) = -\omega G'_s(\omega) \ge 0, \quad \omega \in \mathbb{R}, \tag{2.22}$$

where the inequality is a consequence of $(2.19)_1$. The quantity $H(\omega)$ goes to zero at least quadratically at the origin. It is assumed that the behaviour is in fact quadratic, i.e. $H(\omega)/\omega^2$ tends to a finite, non-zero quantity as ω tends to zero.

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

$$H(\omega) = H_+(\omega)H_-(\omega), \tag{2.23}$$

where $H_+(\omega)$ has no singularities or zeros in $W^{(-)}$ and is thus analytic in Ω^-. Similarly, $H_-(\omega)$ is analytic in Ω^+ with no zeros in $W^{(+)}$. That such a factorization is always possible was shown for general tensor constitutive relations in [7].

Using (2.18) and (2.22), one can show that

$$H_\infty = \lim_{|\omega|\to\infty} H(\omega) = -G'(0) \ge 0. \tag{2.24}$$

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

The factorization (2.23) is unique up to a constant phase factor. We put [16]

$$\begin{gathered} H_{\pm}(\omega) = H_{\mp}(-\omega) = \overline{H_{\mp}}(\omega), \\ H(\omega) = |H_{\pm}(\omega)|^2. \end{gathered} \tag{2.25}$$

A general method is outlined in [16] for determining the factors of H, though for the case of discrete spectrum materials, one can deduce $H_{\pm}$ by inspection.

The factorization (2.23) is the one relevant to the minimum free energy. We shall require a much broader class of factorizations, where the property that the zeros of $H_{\pm}(\omega)$ are in $\Omega^{(\pm)}$ respectively need not be true. These generate a range of free energies related to the minimum free energy, as discussed in subsection 3.5.

3. Detailed forms of the various functionals

3.1. **The work function.**

The work function $(2.8)_1$ can be put in various forms ([2] and earlier references cited therein), including

$$\begin{aligned} W(t) &= \phi(t) + \frac{1}{2}\int_0^\infty \int_0^\infty G_{12}(|s-u|)E_r^t(u)E_r^t(s)duds \\ &= \phi(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty} H(\omega)|E_{r+}^t(\omega)|^2 d\omega, \end{aligned} \tag{3.1}$$

where E_{r+}^t is the Fourier transform of E_r^t, defined by $(2.2)_2$ for $s \in \mathbb{R}^+$ and zero for $s \in \mathbb{R}^{--}$. This transform is given by

$$E_{r+}^t(\omega) = E_+^t(\omega) - \frac{E(t)}{i\omega^-} \tag{3.2}$$

and $E_+^t(\omega)$ is an example of $(2.15)_2$. The notation $\omega^{\pm}$, which will also occur in (3.28) below, was introduced in [16] and used in subsequent work. It implies that ω is moved slightly off the real axis to either of $\omega \pm i\epsilon$ before integrations are carried out and restored afterwards to achieve a finite result. The form given by $(3.1)_2$ is manifestly non-negative.

We see that $W(t)$ can be cast in the form (2.1) by putting

$$G_{12}(s,u) = G_{12}(|s-u|). \tag{3.3}$$

Thus, $W(t)$ can be regarded as a free energy, but with zero dissipation, which is clear from $(2.8)_1$ and (2.7). Because of the vanishing dissipation, it must be the maximum free energy associated with the material or greater than this quantity, an observation which follows from (2.7). Both of these situations can occur, depending on whether the minimal state is a singleton or not [17, 18]. Clearly, of course, zero dissipation is non-physical for a material with memory.

We now present functionals that are free energies provided certain assumptions on the relaxation function are valid. Two examples of quadratic functionals will be explored which are free energies only for a sub-category (though an important one) of materials, namely those with the property

$$G'(s) \le 0, \quad G''(s) \ge 0, \quad \forall s \in \mathbb{R}^+. \tag{3.4}$$

A third example (subsection 3.3 below) requires complete monotonicity for $G(s)$, which means that [5]

$$(-1)^n G^{(n)}(s) \ge 0, \quad n = 1, 2, \dots, \tag{3.5}$$

where $G^{(n)}(s)$ is the nth derivative with respect to s. Relations (3.4) clearly hold for the forms of the relaxation function relating to discrete spectrum materials, as described in section 4. Complete monotonicity is a stronger constraint than (3.4) but is also satisfied for discrete spectrum materials.

3.2. **Graffi-Volterra free energy.** Let us first present the Graffi-Volterra functional [19, 21, 6, 5]

$$\psi_G(t) = \phi(t) - \frac{1}{2}\int_0^\infty G'(s)[E_r^t(s)]^2\, ds. \tag{3.6}$$

The rate of dissipation associated with ψ_G can be determined from (2.6) to have the form

$$D_G(t) = \frac{1}{2}\int_0^\infty G''(s)[E_r^t(s)]^2 ds. \tag{3.7}$$

These quantities are non-negative under assumption (3.4). Thus (3.6) is a free energy if (3.4) holds.

The Graffi-Volterra free energy is a functional of the minimal state if the material is such that the minimal states are singletons, in other words, if the minimal state is simply $(E^t, E(t))$. This is not true for discrete spectrum materials [8, 17].

If the relaxation function G has the property that there exists $\alpha_m \in \mathbb{R}^{++}$ such that

$$G''(s) + \alpha_m G'(s) \geq 0, \quad s \in \mathbb{R}^+, \tag{3.8}$$

then it is easy to show from (3.6) and (3.7) that

$$D_G(t) \geq \alpha_m[\psi_G(t) - \phi(t)]. \tag{3.9}$$

For the discrete spectrum case introduced in section 4 below, there is a minimum inverse decay time $\alpha_{\min} > 0$ and any choice α with the property that

$$0 < \alpha \leq \alpha_{\min} \tag{3.10}$$

obeys (3.9). Property (3.9), which holds for all the free energy functionals considered in this work, is useful in certain theoretical contexts [8, 2].

If there exists $\alpha_M \in \mathbb{R}^{++}$ such that

$$G''(s) + \alpha_M G'(s) \leq 0, \quad s \in \mathbb{R}^+, \tag{3.11}$$

then we have

$$D_G(t) \leq \alpha_M[\psi_G(t) - \phi(t)]. \tag{3.12}$$

For the discrete spectrum case, there is a maximum inverse decay time $\alpha_{\max} > 0$ and a suitable choice of α_M is any $\alpha \in \mathbb{R}^{++}$ such that

$$\alpha \geq \alpha_{\max}. \tag{3.13}$$

The functionals ψ_G and D_G can be put in the form (2.1) and (2.10) respectively [2].

3.3. **Dill free energy.** The functional (cf. (2.1))

$$\psi_{\mathrm{Dill}}(t) = \phi(t) + \frac{1}{2}\int_0^\infty \int_0^\infty G''(s_1+s_2)E_r^t(s_2)E_r^t(s_1)\,ds_1\,ds_2 \tag{3.14}$$

is a free energy with rate of dissipation (cf. (2.10)) given by

$$D_{\mathrm{Dill}}(t) = -\int_0^\infty \int_0^\infty G'''(s_1+s_2)E_r^t(s_2)E_r^t(s_1)\,ds_1\,ds_2 \tag{3.15}$$

if and only if G is completely monotonic, as defined by (3.5).

It can be shown that [1, 2]

$$\psi_{\mathrm{Dill}}(t) \le \psi_G(t), \quad t \in \mathbb{R}. \tag{3.16}$$

The quantity ψ_{Dill} is a functional of the minimal state.

If a quantity α_m obeys (3.10) and α_M obeys (3.13) then [1]

$$G'''(s) + \alpha_m G''(s) \le 0, \quad G'''(s) + \alpha_M G''(s) \ge 0, \quad s \in \mathbb{R}^+, \tag{3.17}$$

which in turn yield

$$D_{\mathrm{Dill}}(t) \ge 2\alpha_m[\psi_{\mathrm{Dill}}(t) - \phi(t)] \ge \alpha_m[\psi_{\mathrm{Dill}}(t) - \phi(t)], \tag{3.18}$$

$$D_{\mathrm{Dill}}(t) \le 2\alpha_M[\psi_{\mathrm{Dill}}(t) - \phi(t)]. \tag{3.19}$$

Relation $(3.18)_1$ is a stronger lower bound than (3.9). However, (3.19) is a weaker upper bound than (3.12).

3.4. **An explicit functional of the minimal state.** We now explore a functional which is a free energy for materials with the property (3.4) and is a functional of the minimal state. These results were first reported in [8]. Consider the quantity

$$\begin{gathered} \psi_F(t) = \phi(t) - \frac{1}{2}\int_0^\infty \frac{[\dot{I}^t(\tau)]^2}{G'(\tau)}d\tau, \\ \dot{I}^t(\tau) = \frac{\partial}{\partial\tau}I^t(\tau), \quad I^t(\tau) = I(\tau, E_r^t), \end{gathered} \tag{3.20}$$

with $I(\tau, E_r^t)$ defined by

$$I(\tau, E_r^t) = \int_0^\infty G'(\tau+u)E_r^t(u)du = \int_0^\infty G'(\tau+u)E^t(u)du + \breve{G}(\tau)E(t), \tag{3.21}$$

where

$$\breve{G}(\tau) = G(\tau) - G_\infty. \tag{3.22}$$

Note the property

$$\lim_{\tau\to\infty} I(\tau, E_r^t) = 0. \tag{3.23}$$

We have

$$\dot{I}^t(\tau) = \int_0^\infty G''(\tau+u)E_r^t(u)du = \int_0^\infty G'(\tau+u)\frac{d}{dt}E^t(u)du. \tag{3.24}$$

The integral term in (3.20) is non-negative by virtue of $(3.4)_1$. The quantity $(G')^{-1}$ becomes singular at large τ but this is cancelled by the numerator ([8] for example).

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[1] This can be demonstrated for any completely monotonic relaxation function using a general representation for such functions [5, 6]. A simple version of the proof can be given using (4.1) below.

We shall see below how this is manifested for the forms of relaxation function of interest here. The rate of dissipation is given by

$$\begin{aligned} D_F(t) &= -\frac{1}{2}\frac{[\dot{I}^t(0)]^2}{G'(0)} - \frac{1}{2}\int_0^\infty \big[\frac{d}{d\tau}\frac{1}{G'(\tau)}\big][\dot{I}^t(\tau)]^2 d\tau \\ &= -\frac{1}{2}\frac{[\dot{I}^t(0)]^2}{G'(0)} + \frac{1}{2}\int_0^\infty G''(\tau)\big[\frac{\dot{I}^t(\tau)}{G'(\tau)}\big]^2 d\tau \geq 0, \end{aligned} \tag{3.25}$$

which can be deduced from (2.6). The non-negativity property is a consequence of (3.4).

If (3.8) is true, then it follows that

$$D_F(t) \geq \alpha_m[\psi_F(t) - \phi(t)]. \tag{3.26}$$

3.5. **Form of the minimum and related free energies.** It is shown in [11, 17] that, for materials with only isolated singularities, one can write down many factorizations of $H(\omega)$, other than (2.23). We have [17]

$$H(\omega) = H_+^f(\omega)H_-^f(\omega), \quad H_\pm^f(\omega) = H_\mp^f(-\omega) = \overline{H_\mp^f}(\omega), \tag{3.27}$$

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

$$\begin{aligned} \psi_f(t) &= \phi(t) + \frac{1}{2\pi}\int_{-\infty}^\infty |p_-^{ft}(\omega)|^2\, d\omega, \\ p_-^{ft}(\omega) &= \frac{1}{2\pi i}\int_{-\infty}^\infty \frac{H_-^f(\omega')E_{r+}^t(\omega')}{\omega' - \omega^+} d\omega'. \end{aligned} \tag{3.28}$$

Defining

$$K_f(t) = \frac{1}{2\pi}\int_{-\infty}^\infty H_-^f(\omega)E_{r+}^t(\omega)d\omega = \lim_{\omega\to\infty}[-i\omega p_-^{ft}(\omega)], \tag{3.29}$$

we can write the associated rate of dissipation in the form

$$D_f(t) = |K_f(t)|^2. \tag{3.30}$$

All these free energies can be shown to be on the boundary of the convex set of free energies associated with a given state of the material. Also, they are all functionals of the minimal state. The factorization (2.23) yields the minimum free energy $\psi_m(t)$. Each exchange of zeros, starting from these factors, can be shown to yield a free energy which is greater than or equal to the previous one.

A particularly interesting one, which we denote by $\psi_M(t)$, is obtained by interchanging all the zeros. This can be identified as the maximum free energy among all those that are functionals of the minimal state. It is less than the work function, which is not a functional of the minimal state for materials with only isolated singularities [2]. Also, it is not necessarily greater than the Graffi-Volterra free energy, which is not a functional of the minimal state.

Remark 3.1. Some important differences between materials with only isolated singularities (in particular the discrete spectrum case) and those with branch points (in particular the continuous spectrum case) were emphasized in remark 2.3. Another is that for the latter case (branch points present), the functional $\psi_M(t)$ must be identified with the work function, which is an upper limit for all free energies. For isolated singularity materials, we have

$$\psi(t) \leq \psi_M(t) < W(t), \tag{3.31}$$

if $\psi(t)$ is a functional of the minimal state. However, with increasing density of singularities, we should have

$$\psi_M(t) \to W(t). \tag{3.32}$$

It will be shown later that this happens rapidly as the density of isolated singularities increases. Associated with this is the property that $D_M(t) \to 0$, where $D_M(t)$ is the rate of dissipation corresponding to $\psi_M(t)$.

Note that there are several (indeed many, for large n) different exchange pathways leading from the minimum to the maximum free energy.

It is not immediately clear from the general formulae introduced above that if (3.8) and (3.11) are true, then formulae corresponding to (3.9) and (3.12) follow. However, we shall demonstrate in subsection 6.5 below that equivalent or similar properties hold for ψ_f and D_f in the particular case of discrete spectrum materials.

An average of the quantities ψ_f, which we denote by ψ_p, is a special case of a quantity introduced in [17] as a possible candidate for the physical free energy. This is discussed in subsection 6.6.

4. Discrete spectrum materials

The form of the relaxation function considered here is that for discrete spectrum materials which are discussed in remark 2.3.

Consider a material with relaxation function $G(t)$ of the form

$$G(t) = G_\infty + \sum_{i=1}^{n} G_i e^{-\alpha_i t}, \quad G_\infty \geq 0, \tag{4.1}$$

where n is a positive integer. The inverse decay times $\alpha_i \in \mathbb{R}^+$, $i = 1, 2, \dots, n$ and the coefficients G_i are also generally assumed to be positive, this being the simplest way to ensure the condition $(2.19)_1$, which is clear from $(4.5)_3$ below. We arrange that $\alpha_1 < \alpha_2 < \alpha_3 \dots$. The quantities $\alpha_{\min}$ and $\alpha_{\max}$ introduced in subsection 3.2 are given by

$$\alpha_{\min} = \alpha_1, \quad \alpha_{\max} = \alpha_n. \tag{4.2}$$

Differentiating (4.1) yields

$$G'(t) = \sum_{i=1}^{n} g_i e^{-\alpha_i t}, \quad g_i = -\alpha_i G_i < 0. \tag{4.3}$$

Note that

$$G_0 = G_\infty + \sum_{i=1}^{n} G_i = G_\infty - \sum_{i=1}^{n} \frac{g_i}{\alpha_i}. \tag{4.4}$$

From (2.17),

$$G'_+(\omega) = \sum_{i=1}^{n} \frac{g_i}{\alpha_i + i\omega}, \quad G'_c(\omega) = \sum_{i=1}^{n} \frac{\alpha_i g_i}{\alpha_i^2 + \omega^2}, \quad G'_s(\omega) = \omega \sum_{i=1}^{n} \frac{g_i}{\alpha_i^2 + \omega^2}. \tag{4.5}$$

Relation (2.22) gives

$$H(\omega) = -\omega^2 \sum_{i=1}^{n} \frac{g_i}{\alpha_i^2 + \omega^2} \geq 0. \tag{4.6}$$

This quantity can be expressed in the form [16]

$$H(\omega) = H_\infty \prod_{i=1}^{n} \Big\{ \frac{\gamma_i^2 + \omega^2}{\alpha_i^2 + \omega^2} \Big\}, \tag{4.7}$$

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

$$\gamma_1 = 0, \quad \alpha_1^2 < \gamma_2^2 < \alpha_2^2 < \gamma_3^2 \dots . \tag{4.8}$$

5. Sinusoidal and exponential histories

Our ultimate aim in this work is to give detailed expressions and numerical examples for the various free energies described in section 3 in the case of discrete spectrum materials and for specified histories. Two types of history will be studied in detail, namely those with sinusoidal and exponential behaviour respectively. The former are always of interest in applications. The latter are mathematically convenient and, over short intervals of time, approximate linear histories.

One can approach this task from two different directions, which yield results that are superficially quite different. Firstly, one can specialize to specific histories, maintaining a general relaxation function. Interesting expressions emerge which can then be specialized to the case of particular relaxation functions. Alternatively, one can consider a particular relaxation function, for example, the discrete spectrum form and determine expressions for general histories. These can then be specialized to the specific histories of interest. It is fairly straightforward to reconcile the formulae from the two approaches in most cases. This is not true however for the quantities $\psi_f(t)$, given by (3.28). It will be seen that some difficult algebra is required to reconcile the formulae relating to these free energies.

Let us refer to the two approaches outlined above as (a) and (b).

For a discrete spectrum material specified by (4.1), we have (approach (b))

$$T(t) = G_0 E(t) + \sum_{i=1}^{n} g_i E_+^t(-i\alpha_i), \tag{5.1}$$

where $(2.4)_2$ has been used. Note that $E_+^t(-i\alpha)$ is the Laplace transform of $E^t(s)$ which we will also denote by $E_L^t(\alpha)$. It is given by

$$E_+^t(-i\alpha) = E_L^t(\alpha) = \int_0^\infty e^{-\alpha u} E^t(u) du. \tag{5.2}$$

Also, the Laplace transform of $E_r^t(s)$ is defined by (see (3.2))

$$E_{r+}^t(-i\alpha) = E_{rL}^t(\alpha) = \int_0^\infty e^{-\alpha u} E_r^t(u) du = E_+^t(-i\alpha) - \frac{E(t)}{\alpha}. \tag{5.3}$$

5.1. **Sinusoidal histories.** Some formulae from [1, 2] for sinusoidal histories are adapted to the scalar case, and presented below.

Consider a history and current value $(E^t, E(t))$ defined by

$$E(t) = E_0 e^{i\omega_- t} + \overline{E_0} e^{-i\omega_+ t}, \quad E^t(s) = E(t-s), \tag{5.4}$$

where E_0 is an amplitude and $\overline{E_0}$ its complex conjugate. Furthermore,

$$\omega_- = \omega_0 - i\eta, \quad \omega_+ = \overline{\omega}_-, \quad \omega_0, \eta \in \mathbb{R}^{++}. \tag{5.5}$$

The parameter η is introduced to ensure finite results in certain quantities. The quantity E^t_+ has the form

$$E^t_+(\omega) = E_0 \frac{e^{i\omega_- t}}{i(\omega + \omega_-)} + \overline{E_0} \frac{e^{-i\omega_+ t}}{i(\omega - \omega_+)}. \tag{5.6}$$

and the Fourier transform of the relative history $E^t_r(s) = E^t(s) - E(t)$, namely $E^t_{r+}(\omega)$ (see (3.2); also (5.3)), is given by

$$E^t_{r+}(\omega) = E^t_+(\omega) - \frac{E(t)}{i\omega^-} = -E_0 \frac{\omega_-}{\omega^-} \frac{e^{i\omega_- t}}{i(\omega + \omega_-)} + \overline{E_0} \frac{\omega_+}{\omega^-} \frac{e^{-i\omega_+ t}}{i(\omega - \omega_+)}. \tag{5.7}$$

From $(2.4)_2$ we have (approach (a))

$$T(t) = [G_0 + G'_+(\omega_-)]E_0 e^{i\omega_- t} + [G_0 + G'_+(-\omega_+)]\overline{E_0} e^{-i\omega_+ t}. \tag{5.8}$$

Referring to (5.2) and (5.6), we see that

$$E^t_+(-i\alpha) = E^t_L(\alpha) = E_0 \frac{e^{i\omega_- t}}{\alpha + i\omega_-} + \overline{E_0} \frac{e^{-i\omega_+ t}}{\alpha - i\omega_+}. \tag{5.9}$$

From (5.3) and (5.9),

$$E^t_{r+}(-i\alpha) = E^t_{rL}(\alpha) = -iE_0 \frac{\omega_-}{\alpha} \frac{e^{i\omega_- t}}{\alpha + i\omega_-} + i\overline{E_0} \frac{\omega_+}{\alpha} \frac{e^{-i\omega_+ t}}{\alpha - i\omega_+}, \tag{5.10}$$

where (5.7) may also be used.

We see that (5.1) agrees with (5.8), by the relation

$$G'_+(\omega_-)E_0 e^{i\omega_- t} + G'_+(-\omega_+)\overline{E_0} e^{-i\omega_+ t} = \sum_{i=1}^{n} g_i E^t_+(-i\alpha_i), \tag{5.11}$$

which follows from $(4.5)_1$ and (5.9).

In the limit $\eta \to 0$, any real algebraic quadratic form in $E(t)$ or real functional quadratic form in $E^t(s)$ can be written as

$$V = ME_0^2 e^{2i\omega_0 t} + \overline{M}\,\overline{E_0}^2 e^{-2i\omega_0 t} + N|E_0|^2, \tag{5.12}$$

The quantity N must be real. Let us introduce the abbreviated notation

$$V = \{M, N\}, \tag{5.13}$$

with properties

$$\begin{gathered} a\{M, N\} = \{aM, aN\}, \\ \{aM_1 + bM_2, aN_1 + bN_2\} = a\{M_1, N_1\} + b\{M_2, N_2\}, \end{gathered} \tag{5.14}$$

for any real a, b. These will be extensively used below. If V is restricted to be non-negative, as in the present context, then the conditions

$$N \geq 0, \quad 2|M| \leq N, \tag{5.15}$$

must apply. The first relation follows by taking a time average over a cycle, the second by expressing the first two terms in (5.12) in polar form and combining them into a cosine function.

Consider the quantity

$$\begin{aligned} &T(t)\dot{E}(t)\\ &= i\omega_-[G_0+G'_+(\omega_-)]E_0^2e^{2i\omega_- t} - i\omega_+[G_0+G'_+(-\omega_+)]\overline{E_0}^2e^{-2i\omega_+ t}\\ &\quad + i[(\omega_- - \omega_+)G_0 + \omega_- G'_+(-\omega_+) - \omega_+ G'_+(\omega_-)]|E_0|^2 e^{i(\omega_- - \omega_+)t}. \end{aligned} \tag{5.16}$$

In the limit $\eta \to 0$, this converges to a finite result of the form

$$T(t)\dot{E}(t) = \{i\omega_0[G_0+G'_+(\omega_0)], -2\omega_0 G'_s(\omega_0)\} \tag{5.17}$$

in the notation of (5.13).

5.2. **Exponential histories.** In this case, we consider a history and current value $(E^t, E(t))$ given by

$$E(t) = E_1 e^{\lambda t}, \quad E^t(s) = E(t-s), \tag{5.18}$$

where E_1 is a constant amplitude. Then, from (5.2) and (5.3), we have

$$\begin{aligned} E^t_+(-i\alpha) &= E^t_L(\alpha) = \frac{E_1 e^{\lambda t}}{\lambda+\alpha} = \frac{E(t)}{\lambda+\alpha},\\ E^t_{r+}(-i\alpha) &= E^t_{rL}(\alpha) = -\frac{\lambda E(t)}{(\lambda+\alpha)\alpha}. \end{aligned} \tag{5.19}$$

The stress function, given by $(2.4)_2$, has the form

$$T(t) = [G_0 + L(\lambda)]E(t), \quad L(\lambda) = G'_+(-i\lambda), \tag{5.20}$$

where the quantity $G'_+(-i\lambda)$ is real and of course equal to the Laplace transform of $G'(s)$. From (5.20), we have

$$T(t)\dot{E}(t) = \frac{1}{2}[G_0 + L(\lambda)]\frac{d}{dt}E^2(t). \tag{5.21}$$

For discrete spectrum materials, it follows from $(4.5)_1$ that

$$L(\lambda) = \sum_{i=1}^n \frac{g_i}{\alpha_i + \lambda}\,. \tag{5.22}$$

It may be seen that (5.1) (approach (b)) agrees with (5.20) (approach (a)) by virtue of the relation

$$L(\lambda)E(t) = \sum_{i=1}^n g_i E^t_+(-i\alpha_i). \tag{5.23}$$

Remark 5.1. Observe that $T(t)$, given by (5.20) is equal to the first term of (5.8) (for $\eta = 0$) at $\omega_0 = -i\lambda$. A similar remark applies to any linear functional of the strain history. Also, there is a general property of quadratic forms in the strain history that if M in (5.13) is equal to $M(\omega_0)$ then the corresponding quantity to V for exponential histories is given by $M(-i\lambda)E^2(t)$. This can be shown by considering the general functionals (2.1) and (2.10) for sinusoidal and exponential histories.

6. Free energy functionals for given histories

6.1. **The work function.** Let us first consider the sinusoidal case.

6.1.1. *Sinusoidal histories.* The work $W(t)$ done on the material to achieve the state $(E^t, E(t))$ is obtained by integrating the form (5.16). We obtain

$$\begin{aligned} W(t) &= \frac{1}{2}\big[[G_0 + G'_+(\omega_-)]E_0^2 e^{2i\omega_- t} + [G_0 + G'_+(-\omega_+)]\overline{E_0}^2 e^{-2i\omega_+ t}\big] \\ &\quad + \big[(\omega_- - \omega_+)G_0 + \omega_- G'_+(-\omega_+) - \omega_+ G'_+(\omega_-)\big]\, |E_0|^2 \frac{e^{i(\omega_- - \omega_+)t}}{(\omega_- - \omega_+)}. \end{aligned} \tag{6.1}$$

This quantity diverges as $\eta \to 0$, as would be expected on physical grounds. Taking the limit $\eta \to 0$ in the terms which are convergent, and using (4.5), we can write this [1, 2] in the notation of (5.13):

$$\begin{gathered} W(t) = \{M, N\}, \\ M = \frac{1}{2}\left[G_0 + G'_+(\omega_0)\right] = \frac{1}{2}\Big[G_0 + \sum_{i=1}^{n} \frac{g_i}{\alpha_i + i\omega_0}\Big], \\ \begin{aligned} N &= G_0 + G'_c(\omega_0) - \omega_0 \frac{\partial}{\partial \omega_0} G'_c(\omega_0) - \omega_0 G'_s(\omega_0)\big(2t + \frac{1}{\eta}\big) \\ &= G_0 + \sum_{i=1}^{n} \frac{\alpha_i g_i}{\alpha_i^2 + \omega_0^2} + 2\omega_0^2 \sum_{i=1}^{n} \frac{\alpha_i g_i}{(\alpha_i^2 + \omega_0^2)^2} - \omega_0^2 \sum_{i=1}^{n} \frac{g_i}{\alpha_i^2 + \omega_0^2}\big(2t + \frac{1}{\eta}\big). \end{aligned} \end{gathered} \tag{6.2}$$

This is approach (a). To adopt (b), we use (5.9) in (5.1) and determine $\dot{E}(t)$ from (5.4). It is easy to show that the expression for M agrees with (6.2). To reconcile the expression for N requires a little more algebra. One must show that

$$\begin{aligned} &\frac{1}{\omega_- - \omega_+}\big[\frac{\omega_-}{\alpha_i - i\omega_+} - \frac{\omega_+}{\alpha_i + i\omega_-}\big] \\ &\approx \frac{\alpha_i}{\alpha_i^2 + \omega_0^2} - \frac{\omega_0^2}{\eta} \frac{1}{(\alpha_i + \eta)^2 + \omega_0^2} \\ &= \frac{\alpha_i}{\alpha_i^2 + \omega_0^2} - \omega_0^2 \big[\frac{\partial}{\partial \eta} \frac{1}{(\alpha_i + \eta)^2 + \omega_0^2}\big]\big|_{\eta=0} - \frac{1}{\eta} \frac{\omega_0^2}{\alpha_i^2 + \omega_0^2}. \end{aligned} \tag{6.3}$$

6.1.2. *Exponential histories.* Integrating (5.21) over all past history gives

$$W(t) = \frac{1}{2}[G_0 + L(\lambda)]E^2(t) = \frac{1}{2}\Big[G_0 + \sum_{i=1}^{n} \frac{g_i}{\alpha_i + \lambda}\Big] E_1^2 e^{2\lambda t}. \tag{6.4}$$

We see that this formula is an example of the property noted in remark 5.1. Several other examples are presented below.

6.2. **Graffi-Volterra equation.** Adopting approach (b), we have, using (3.6) and (4.3),

$$\psi_G(t) = \phi(t) - \frac{1}{2} \sum_{i=1}^{n} g_i E^t_{sLr}(\alpha_i), \quad D_G(t) = -\frac{1}{2} \sum_{i=1}^{n} \alpha_i g_i E^t_{sLr}(\alpha_i), \tag{6.5}$$

where $E^t_{sLr}(\alpha)$ denotes the Laplace transform of $[E^t_r(s)]^2$, given by

$$E^t_{sLr}(\alpha) = \int_0^\infty e^{-\alpha s} [E^t_r(s)]^2 ds = E^t_{sL}(\alpha) - 2E(t) E^t_L(\alpha) + \frac{E^2(t)}{\alpha}, \tag{6.6}$$

and $E^t_{sL}(\alpha)$ denotes the Laplace transform of $[E^t(s)]^2$,

$$E^t_{sL}(\alpha) = \int_0^\infty e^{-\alpha s} [E^t(s)]^2 ds. \tag{6.7}$$

The quantity $E^t_L(\alpha)$ is defined by (5.9) or (5.19).

Let us now consider approach (a).

6.2.1. *Sinusoidal histories.* Relation (3.6) has the form [1]

$$\begin{aligned}\psi_G(t)&\\&=\Big\{\frac{1}{2}G_0+G'_+(\omega_0)-\frac{1}{2}G'_+(2\omega_0),2G_0-G_\infty+2G'_c(\omega_0)\Big\}\\&=\Big\{\frac{1}{2}G_0+\sum_{i=1}^n\frac{g_i}{\alpha_i+i\omega_0}-\frac{1}{2}\sum_{i=1}^n\frac{g_i}{\alpha_i+2i\omega_0},2G_0-G_\infty+2\sum_{i=1}^n\frac{\alpha_i g_i}{\alpha_i^2+\omega_0^2}\Big\},\end{aligned}\tag{6.8}$$

so that the time average of ψ_G over a cycle is

$$\langle\psi_G(t)\rangle_{av}=[2G_0-G_\infty+2G'_c(\omega_0)]|E_0|^2=\Big[2G_0-G_\infty+2\sum_{i=1}^n\frac{\alpha_i g_i}{\alpha_i^2+\omega_0^2}\Big]|E_0|^2.\tag{6.9}$$

Also,

$$\begin{aligned}D_G(t)&=\{-i\omega_0[G'_+(\omega_0)-G'_+(2\omega_0)],-2\omega_0G'_s(\omega_0)\}\\&=\Big\{-i\omega_0\Big[\sum_{i=1}^n\frac{g_i}{\alpha_i+i\omega_0}-\sum_{i=1}^n\frac{g_i}{\alpha_i+2i\omega_0}\Big],-2\omega_0^2\sum_{i=1}^n\frac{g_i}{\alpha_i^2+\omega_0^2}\Big\}.\end{aligned}\tag{6.10}$$

It is shown in [1] that the second parameter in the rate of dissipation is always $-2\omega_0G'_s(\omega_0)$. Note that

$$\phi(t)=\big\{\frac{1}{2}G_\infty,G_\infty\big\}.\tag{6.11}$$

The Laplace transform (6.7) has the form

$$\begin{aligned}E^t_{sL}(\alpha)&=\big\{\frac{1}{\alpha+2i\omega_0},\frac{2}{\alpha}\big\},\\E^t_{sLr}(\alpha)&=\big\{\frac{1}{\alpha+2i\omega_0}-\frac{2}{\alpha+i\omega_0}+\frac{1}{\alpha},\frac{4}{\alpha}-\frac{4\alpha}{\alpha^2+\omega_0^2}\big\},\end{aligned}\tag{6.12}$$

where (5.9) has been used. Recalling (4.4), we see that (6.5) agrees with $(6.8)_2$ and $(6.10)_2$.

6.2.2. *Exponential histories.* In this case, we have (approach (a))

$$\begin{aligned}\psi_G(t)&=\big[\frac{1}{2}G_0+L(\lambda)-\frac{1}{2}L(2\lambda)\big]E^2(t)\\&=\Big[\frac{1}{2}G_0+\sum_{i=1}^n\frac{g_i}{\alpha_i+\lambda}-\frac{1}{2}\sum_{i=1}^n\frac{g_i}{\alpha_i+2\lambda}\Big]E^2(t),\\D_G(t)&=-\lambda[L(\lambda)-L(2\lambda)]E^2(t)\\&=-\lambda\Big[\sum_{i=1}^n\frac{g_i}{\alpha_i+\lambda}-\sum_{i=1}^n\frac{g_i}{\alpha_i+2\lambda}\Big]E^2(t),\end{aligned}\tag{6.13}$$

which can be shown to be equal to the results from (6.5) (approach (b)). These provide another example of remark 5.1.

6.3. **Dill free energy.** We next consider the expression (3.14) for the Dill free energy. Adopting approach (b), we have

$$\psi_{\mathrm{Dill}}(t) = \phi(t) - \frac{1}{2}\sum_{i=1}^{n} \alpha_i g_i [E^t_{rL}(\alpha_i)]^2 \tag{6.14}$$

where E^t_{rL} is defined by (5.10) in the limit $\eta \to 0$, or $(5.19)_2$. The rate of dissipation (3.15) is given by

$$D_{\mathrm{Dill}}(t) = -\sum_{i=1}^{n} \alpha_i^2 g_i [E^t_{rL}(\alpha_i)]^2. \tag{6.15}$$

Now consider approach (a).

6.3.1. *Sinusoidal histories.* For this case, we have [1]

$$\begin{aligned}\psi_{\mathrm{Dill}}(t) &\\ = \Big\{ \frac{1}{2}[G_0 + G'_+(\omega_0) - \omega_0 \frac{\partial}{\partial\omega_0} G'_+(\omega_0)], G_0 + G'_c(\omega_0)\Big\}, &\\ = \Big\{ \frac{1}{2}\Big[G_0 + \sum_{i=1}^{n} \frac{g_i}{\alpha_i + i\omega_0} + i\omega_0 \sum_{i=1}^{n} \frac{g_i}{(\alpha_i + i\omega_0)^2}\Big], G_0 + \sum_{i=1}^{n} \frac{\alpha_i g_i}{\alpha_i^2 + \omega_0^2}\Big\}, &\end{aligned} \tag{6.16}$$

so that

$$\langle \psi_{\mathrm{Dill}}(t)\rangle_{av} = [G_0 + G'_c(\omega_0)]|E_0|^2 = \Big[G_0 + \sum_{i=1}^{n} \frac{\alpha_i g_i}{\alpha_i^2 + \omega_0^2}\Big]|E_0|^2. \tag{6.17}$$

Relation (3.16) averaged over a cycle and applied to (6.9), (6.17), is equivalent to the inequality

$$G_0 + G'_c(\omega_0) \geq G_\infty. \tag{6.18}$$

This is an equality at $\omega_0 = 0$, by virtue of (4.4) and $(4.5)_2$, while $G'_c(\omega_0)$, a negative quantity, decreases in magnitude for increasing ω_0, as we see from $(6.17)_2$. Relation (6.18) is in fact the general requirement (2.3), applied to (6.17). Also,

$$\begin{aligned} D_{\mathrm{Dill}}(t) &= \Big\{ i\omega_0^2 \frac{\partial}{\partial\omega_0} G'_+(\omega_0), -2\omega_0 G'_s(\omega_0)\Big\} \\ &= \Big\{ \omega_0^2 \sum_{i=1}^{n} \frac{g_i}{(\alpha_i + i\omega_0)^2}, -2\omega_0^2 \sum_{i=1}^{n} \frac{g_i}{\alpha_i^2 + \omega_0^2}\Big\}, \end{aligned} \tag{6.19}$$

where again we see that the second parameter is $-2\omega_0 G'_s(\omega_0)$.

Note that

$$[E^t_{rL}(\alpha)]^2 = \frac{\omega_0^2}{\alpha^2}\Big\{ -\frac{1}{(\alpha + i\omega_0)^2}, \frac{2}{\alpha^2 + \omega_0^2}\Big\}. \tag{6.20}$$

Using (6.20) and (4.4), we see that there is agreement between (6.14) and (6.16).

6.3.2. *Exponential histories.* Recalling remark 5.1, together with (6.16) and (6.19), we have (approach (a))

$$\begin{aligned}
\psi_{\mathrm{Dill}}(t) &= \frac{1}{2}[G_0 + L(\lambda) - \lambda\frac{\partial}{\partial\lambda}L(\lambda)]E^2(t) \\
&= \frac{1}{2}\Big[G_0 + \sum_{i=1}^{n}\frac{g_i}{\alpha_i+\lambda} + \lambda\sum_{i=1}^{n}\frac{g_i}{(\alpha_i+\lambda)^2}\Big]E^2(t), \qquad (6.21)\\
D_{\mathrm{Dill}}(t) &= \lambda^2\frac{\partial}{\partial\lambda}L(\lambda)E^2(t) = -\Big[\lambda^2\sum_{i=1}^{n}\frac{g_i}{(\alpha_i+\lambda)^2}\Big]E^2(t),
\end{aligned}$$

which can be shown to be equal to (6.14) and (6.15) (approach (b)) with the aid of (4.4) and (5.19). One can show that (3.16) holds.

6.4. **The functional ψ_F.** Next, let us consider ψ_F, given by (3.20). Using approach (b), we put

$$\dot I^t(\tau) = -\sum_{i=1}^{n}\alpha_i g_i e^{-\alpha_i\tau}E^t_{rL}(\alpha_i) = \sum_{i=1}^{n}h_i e^{-\alpha_i\tau}, \quad h_i = -\alpha_i g_i E^t_{rL}(\alpha_i), \qquad (6.22)$$

where E^t_{rL} is given by (5.10) or (5.19). Thus, we can write $(3.20)_1$ in the forms

$$\begin{aligned}
\psi_F(t) &= \phi(t) - \frac{1}{2}\int_0^\infty \frac{[\sum_{i=1}^{n}h_i e^{-\alpha_i\tau}]^2}{\sum_{i=1}^{n}g_i e^{-\alpha_i\tau}}d\tau \\
&= \phi(t) - \frac{1}{2}\int_0^\infty \frac{[\sum_{i=1}^{n}h_i e^{(\alpha_1-\alpha_i)\tau}][\sum_{i=1}^{n}h_i e^{-\alpha_i\tau}]}{\sum_{i=1}^{n}g_i e^{(\alpha_1-\alpha_i)\tau}}d\tau.
\end{aligned} \qquad (6.23)$$

The advantage of writing it in the second form, obtained by multiplying the numerator and denominator by $e^{\alpha_1\tau}$, is that the denominator now goes to the limit g_1 at large τ, instead of zero. Also, from (3.25),

$$\begin{aligned}
D_F(t) &= -\frac{1}{2}\frac{[\sum_{i=1}^{n}h_i]^2}{\sum_{i=1}^{n}g_i} - \frac{1}{2}\int_0^\infty\sum_{i=1}^{n}\alpha_i g_i e^{-\alpha_i\tau}\Big[\frac{\sum_{i=1}^{n}h_i e^{-\alpha_i\tau}}{\sum_{i=1}^{n}g_i e^{-\alpha_i\tau}}\Big]^2 d\tau, \\
&= -\frac{1}{2}\frac{[\sum_{i=1}^{n}h_i]^2}{\sum_{i=1}^{n}g_i} - \frac{1}{2}\int_0^\infty\sum_{i=1}^{n}\alpha_i g_i e^{-\alpha_i\tau}\Big[\frac{\sum_{i=1}^{n}h_i e^{(\alpha_1-\alpha_i)\tau}}{\sum_{i=1}^{n}g_i e^{(\alpha_1-\alpha_i)\tau}}\Big]^2 d\tau.
\end{aligned} \qquad (6.24)$$

Consider now approach (a).

6.4.1. *Sinusoidal histories.* We have, from (3.24),

$$\begin{aligned}
\dot I^t(s) &= F(\omega_0,s)E_0e^{i\omega_0t} + \overline{F}(\omega_0,s)\overline{E_0}e^{-i\omega_0t}, \\
F(\omega_0,s) &= \int_0^\infty G''(u+s)(e^{-i\omega_0u}-1)du \\
&= \int_0^\infty G''(u+s)e^{-i\omega_0u}du + G'(s) \\
&= i\omega_0\int_0^\infty G'(u+s)e^{-i\omega_0u}du.
\end{aligned} \qquad (6.25)$$

Observe that

$$\overline{F}(\omega_0,s) = F(-\omega_0,s). \qquad (6.26)$$

The relations

$$F(\omega_0,0) = G''_+(\omega_0) + G'(0) = i\omega_0G'_+(\omega_0) \qquad (6.27)$$

will be useful. In the notation (5.13), we have

$$\psi_F(t) - \phi(t) = -\Big\{\frac{1}{2}\int_0^\infty \frac{[F(\omega_0, s)]^2}{G'(s)}\,ds, \int_0^\infty \frac{|F(\omega_0, s)|^2}{G'(s)}\,ds\Big\} \tag{6.28}$$

Thus, $\langle\psi_F(t)\rangle_{av}$ is given by

$$\langle\psi_F(t)\rangle_{av} = \Big[G_\infty - \int_0^\infty \frac{|F_s(\omega_0, s)|^2}{G'(s)}\,ds\Big]|E_0|^2. \tag{6.29}$$

Also,

$$D_F(t) = \Big\{\frac{\omega_0^2}{2}\frac{[G'_+(\omega_0)]^2}{G'(0)} + \frac{1}{2}\int_0^\infty G''(s)\big[\frac{F(\omega_0, s)}{G'(s)}\big]^2\,ds, -2\omega_0 G'_s(\omega_0)\Big\}, \tag{6.30}$$

where, as noted earlier, the form of the second parameter follows from general arguments [1].

For a discrete spectrum material,

$$F(\omega_0, s) = i\omega_0 \sum_{i=1}^n \frac{g_i e^{-\alpha_i s}}{\alpha_i + i\omega_0}, \tag{6.31}$$

which follows both from (6.25) (approach (a)) and (6.22) (approach (b)).

For sinusoidal histories, $E^t_{rL}(\alpha)$ is defined by (5.10). Then, we see that (6.23) and (6.28) are in agreement as are (6.24) and (6.30).

6.4.2. *Exponential histories.* Adopting approach (a), we have from $(3.24)_2$ and (4.3) that

$$\dot I^t(s) = \lambda E(t)\int_0^\infty G'(u+s)e^{-\lambda u}du = \lambda E(t)\sum_{i=1}^n \frac{g_i e^{-\alpha_i s}}{\alpha_i + \lambda}. \tag{6.32}$$

Note that, using (6.31), this can be written in the form

$$\dot I^t(s) = F(-i\lambda, s)E(t), \tag{6.33}$$

which is in accordance with Remark 5.1. Relation (6.32) agrees with (6.22) and (5.19), obtained using approach (b). Again using remark 5.1, we see that the quantities $\psi_F(t)$ and $D_F(t)$ are given by

$$\begin{gathered} \psi_F(t) = \phi(t) - \frac{1}{2}\Big\{\int_0^\infty \frac{[F(-i\lambda, s)]^2}{G'(s)}\,ds\Big\}E^2(t), \\ D_F(t) = \Big[-\frac{\lambda^2}{2}\frac{L^2(\lambda)}{G'(0)} + \frac{1}{2}\int_0^\infty G''(s)\big[\frac{F(-i\lambda, s)}{G'(s)}\big]^2\,ds\Big]E^2(t), \end{gathered} \tag{6.34}$$

where $L(\lambda)$ is given by $(5.20)_2$ and, for discrete spectrum materials, (5.22). When the latter expression and (6.31) are substituted into (6.34), they agree with (6.23) and (6.24) (approach (b)), which we see on noting that the coefficients h_i in (6.22) are given by

$$h_i = \frac{\lambda g_i}{\lambda + \alpha_i}. \tag{6.35}$$

6.5. **Minimum and related free energies.** Finally, let us explore the free energies $\psi_f(t)$ given by (3.28).

We first consider sinusoidal histories, using approach (a). Only the minimum free energy is discussed in detail for sinusoidal histories in [1, 2]. However, precisely analogous formulae apply to all the other cases corresponding to the different factorizations discussed after (3.27). Thus, we have

$$\psi_f(t) = \Big\{\frac{1}{2}G_0 + B_1^f(\omega_0), G_0 + B_2^f(\omega_0)\Big\}, \tag{6.36}$$

where

$$\begin{gathered} B_1^f(\omega_0) = \frac{1}{2}\Big\{G'_+(\omega_0) + \frac{i}{\omega_0}[H_-^f(-\omega_0)]^2\Big\} \\ B_2^f(\omega_0) = G'_c(\omega_0) - \omega_0\frac{d}{d\omega_0}G'_c(\omega_0) + Q_f(\omega_0), \end{gathered} \tag{6.37}$$

where $Q_f(\omega)$ is given by

$$Q_f(\omega) = i\Big[\frac{d}{d\omega}H_+^f(\omega)H_-^f(\omega) - H_+^f(\omega)\frac{d}{d\omega}H_-^f(\omega)\Big] \geq 0, \quad \omega \in \mathbb{R}. \tag{6.38}$$

The average over a time cycle is given by

$$\langle\psi_f(t)\rangle_{av} = [G_0 + B_2^f(\omega_0)]|E_0|^2. \tag{6.39}$$

The rate of dissipation is given by (3.30) and (3.29). Thus, we find that

$$K_f(t) = H_-^f(-\omega_0)E_0e^{i\omega_0 t} + H_-^f(\omega_0)\overline{E_0}e^{-i\omega_0 t}, \tag{6.40}$$

yielding

$$D_f(t) = \{[H_-^f(-\omega_0)]^2, 2H(\omega_0)\} = \{[H_+^f(\omega_0)]^2, -2\omega_0 G'_s(\omega_0)\}, \tag{6.41}$$

where $(3.27)_2$ has been used.

Remark 6.1. Note that, from (6.41), the parameter M_f from (5.13) for D_f has magnitude

$$|M_f(t)| = H(\omega_0). \tag{6.42}$$

Thus, the amplitude of the sinusoidal part of D_f is independent of the labeling f. Also, the minimum value of D_f is zero since, referring to (5.15) and (6.41),

$$N_f(t) - 2|M_f| = 0. \tag{6.43}$$

6.5.1. *Exponential histories.* From remark 5.1, we deduce that

$$\psi_f(t) = \frac{1}{2}\Big\{G_0 + L(\lambda) - \frac{1}{\lambda}[H_-^f(i\lambda)]^2\Big\}E^2(t), \quad D_f(t) = [H_-^f(i\lambda)E(t)]^2. \tag{6.44}$$

Next, we adopt approach (b).

6.5.2. *Explicit forms for discrete spectrum materials.* To obtain the minimum free energy, one chooses the factorization of (4.7) given by

$$\begin{gathered} H_+(\omega) = h_\infty\prod_{i=1}^{n}\big\{\frac{\omega - i\gamma_i}{\omega - i\alpha_i}\big\}, \\ H_-(\omega) = h_\infty\prod_{i=1}^{n}\big\{\frac{\omega + i\gamma_i}{\omega + i\alpha_i}\big\}, \quad h_\infty = [H_\infty]^{1/2}. \end{gathered} \tag{6.45}$$

Interchanging the zeros means in effect switching a given γ_i to $-\gamma_i$ in both H_+ and H_-. Let us introduce an n-dimensional vector ϵ_i^f, $i = 1, 2, \dots, n$ where each ϵ_i^f can take values ± 1. We define $\rho_i^f = \epsilon_i^f \gamma_i$, and write

$$H_+^f(\omega) = h_\infty \prod_{i=1}^n \{\frac{\omega - i\rho_i^f}{\omega - i\alpha_i}\}, \quad H_-^f(\omega) = h_\infty \prod_{i=1}^n \{\frac{\omega + i\rho_i^f}{\omega + i\alpha_i}\}. \tag{6.46}$$

Remark 6.2. Each exchange of γ_i and $-\gamma_i$ in $H_+^f(\omega)$ introduces a factor

$$\frac{\omega_0 + i\gamma_i}{\omega_0 - i\gamma_i} = e^{2i\mu_i}, \quad \mu_i = tan^{-1}\frac{\gamma_i}{\omega_0}, \quad \gamma_i, \omega_0 \in \mathbb{R}^{++}, \tag{6.47}$$

where the principal value of $\mu_i \in (0, \pi/2)$. Thus, with each exchange, which will increase the resulting ψ_f, [11, 17, 2], we have the maximum (and all other) points of D_f moving in a negative direction along the time axis.

The most relevant formulae from [11] are now summarized. However, relative histories will be used, rather than histories, as was the case in that reference. By considering the residue at each pole, we find that

$$\begin{gathered} H_-^f(\omega) = h_\infty\Big[1 + i\sum_{i=1}^n \frac{R_i^f}{\omega + i\alpha_i}\Big], \quad H_+^f(\omega) = \overline{H}_-^f(\omega), \\ R_i^f = (\rho_i^f - \alpha_i) \prod_{j=1,\, j\neq i}^n \Big\{\frac{\rho_j^f - \alpha_i}{\alpha_j - \alpha_i}\Big\}. \end{gathered} \tag{6.48}$$

It follows from (6.48) and the fact that H_-^f vanishes at $\omega = 0$ that

$$\sum_{i=1}^n \frac{R_i^f}{\alpha_i} = -1. \tag{6.49}$$

Using (6.49), we can write $H_-^f(\omega)$ in the form

$$H_-^f(\omega) = ih_\infty\omega \sum_{i=1}^n \frac{R_i^f}{\alpha_i(\alpha_i - i\omega)}, \tag{6.50}$$

giving

$$[H_-^f(-\omega)]^2 = -H_\infty\omega^2 \sum_{i,j=1}^n \frac{R_i^f R_j^f}{\alpha_i\alpha_j(\alpha_i + i\omega)(\alpha_j + i\omega)}. \tag{6.51}$$

Also [16, 11]

$$g_i = -2H_\infty \sum_{j=1}^n \frac{R_i^f R_j^f}{(\alpha_i + \alpha_j)\alpha_j}, \tag{6.52}$$

which yields the formula

$$\sum_{i=1}^n \frac{g_i}{\alpha_i} = -2H_\infty \sum_{i,j=1}^n \frac{R_i^f R_j^f}{(\alpha_i + \alpha_j)\alpha_i\alpha_j} = G_\infty - G_0, \tag{6.53}$$

by (4.4) and (6.52). It follows from $(4.5)_1$ that

$$\begin{aligned} &G'_+(\omega_0)\\ &= -2H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{(\alpha_i+\alpha_j)\alpha_j(\alpha_i+i\omega_0)}\\ &= -H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{(\alpha_i+\alpha_j)\alpha_j(\alpha_i+i\omega_o)} - H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{(\alpha_i+\alpha_j)\alpha_i(\alpha_j+i\omega_0)}\\ &= -H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f[2\alpha_i\alpha_j + i\omega_0(\alpha_i+\alpha_j)]}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i+i\omega_0)(\alpha_j+i\omega_0)}. \end{aligned} \tag{6.54}$$

By a similar argument,

$$\begin{gathered} G'_c(\omega_0) - \omega_0 \frac{\partial}{\partial\omega_0} G'_c(\omega_0) = \sum_{i=1}^{n} \alpha_i g_i \frac{\alpha_i^2+3\omega_0^2}{(\alpha_i^2+\omega_0^2)^2}\\ = -H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f N_1^{(ij)}(\omega_0)}{D^{(ij)}(\omega_0)},\\ N_1^{(ij)}(\omega_0) = (\alpha_i^2+3\omega_0^2)\alpha_i^2(\alpha_j^2+\omega_0^2)^2 + (\alpha_j^2+3\omega_0^2)\alpha_j^2(\alpha_i^2+\omega_0^2)^2,\\ D^{(ij)}(\omega_0) = (\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i^2+\omega_0^2)^2(\alpha_j^2+\omega_0^2)^2. \end{gathered} \tag{6.55}$$

Using the expressions (6.50) and its complex conjugate for $H_\pm^f$ and the alternative form (6.48) to calculate derivatives of these quantities, we find that $Q_f(\omega_0)$, defined by (6.38), is given by

$$\begin{gathered} Q_f(\omega_0) = H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f N_2^{(ij)}(\omega_0)}{D^{(ij)}(\omega_0)},\\ N_2^{(ij)}(\omega_0) = (\alpha_1+\alpha_j)^2\omega_0^2[(\alpha_i^2-\omega_0^2)(\alpha_j^2-\omega_0^2) + 4\omega_0^2\alpha_i\alpha_j], \end{gathered} \tag{6.56}$$

and $D^{(ij)}(\omega_0)$ is defined by $(6.55)_4$. The quantity $p_-^{ft}(\omega)$, given by $(3.28)_2$, has the form

$$p_-^{ft}(\omega) = ih_\infty \sum_{i=1}^{n} \frac{R_i^f E_{r+}^t(-i\alpha_i)}{\omega+i\alpha_i}. \tag{6.57}$$

Using (6.57) in $(3.29)_2$, we obtain

$$K_f(t) = h_\infty \Big[\sum_{i=1}^{n} R_i^f E_{r+}^t(-i\alpha_i)\Big]. \tag{6.58}$$

It follows from (6.57) and (3.28) that

$$\psi_f(t) = \phi(t) + H_\infty \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{\alpha_i+\alpha_j} E_{r+}^t(-i\alpha_i) E_{r+}^t(-i\alpha_j), \tag{6.59}$$

where the reality of $E^t_{r+}(-i\alpha_i)$ has been used. Noting (6.58), we see that

$$\begin{aligned} D_f(t) &= H_\infty \Big[\sum_{i=1}^{n} R_i^f E^t_{r+}(-i\alpha_i)\Big]^2 \\ &= H_\infty \sum_{i,j=1}^{n} R_i^f R_j^f E^t_{r+}(-i\alpha_i) E^t_{r+}(-i\alpha_j). \end{aligned} \tag{6.60}$$

Let α_m and α_M have the properties $\alpha_m < \alpha_{\min}$ and $\alpha_M > \alpha_{\max}$, in terms of the quantities introduced in (4.2). Then it follows from (6.59) and (6.60) that

$$D_f(t) \geq 2\alpha_m[\psi_f(t) - \phi(t)] \geq \alpha_m[\psi_f(t) - \phi(t)], \tag{6.61}$$

and

$$D_f(t) \leq 2\alpha_M[\psi_f(t) - \phi(t)]. \tag{6.62}$$

These inequalities are similar to (3.18) and (3.19).

6.5.3. *Sinusoidal histories.* We now derive expressions for ψ_f and D_f, using approach (b). Let us write (6.59) in the notation (5.13), using (5.10) and (6.11),

$$\begin{aligned} \psi_f(t) = \Big\{\frac{1}{2}G_\infty, G_\infty\Big\} + H_\infty \Big\{ &- \sum_{i,j=1}^{n} \frac{R_i^f R_j^f \omega_0^2}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i+i\omega_0)(\alpha_j+i\omega_0)}, \\ & 2\sum_{i,j=1}^{n} \frac{R_i^f R_j^f \omega_0^2(\alpha_i\alpha_j+\omega_0^2)}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i^2+\omega_0^2)(\alpha_j^2+\omega_0^2)}\Big\}. \end{aligned} \tag{6.63}$$

For approach (a), we obtain (6.36) and (6.37). Using (6.51), (6.54), (6.55) and (6.56), we see that (6.36) becomes

$$\begin{aligned} \psi_f(t) = \Big\{\frac{1}{2}G_0, G_0\Big\} - H_\infty \Big\{ &\sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i+i\omega_0)(\alpha_j+i\omega_0)} \\ &\times [((\alpha_i+i\omega_0)(\alpha_j+i\omega_0)+\omega_0^2], \sum_{i,j=1}^{n} \frac{R_i^f R_j^f [N_1^{(ij)}(\omega_0) - N_2^{(ij)}(\omega_0)]}{D^{(ij)}(\omega_0)}\Big\}. \end{aligned} \tag{6.64}$$

With the help of (6.53), one can show, after some algebra, that (6.64) agrees with (6.63).

It is perhaps noteworthy that the elegance of the formula (6.59) contrasts with the comparative inelegance of (6.36). Using (5.10) and (6.50), we have

$$\begin{aligned} &\sum_{i=1}^{n} R_i^f E^t_{r+}(-i\alpha_i) \\ &= -i\omega_0 \sum_{i=1}^{n} \frac{R_i^f}{\alpha_i(\alpha_i+i\omega_0)} E_0 e^{i\omega_0 t} + i\omega_0 \sum_{i=1}^{n} \frac{R_i^f}{\alpha_i(\alpha_i-i\omega_0)} \overline{E_0} e^{-i\omega_0 t} \\ &= \frac{1}{h_\infty}[H_-^f(-\omega_0) E_0 e^{i\omega_0 t} + H_-^f(\omega_0)\overline{E_0} e^{-i\omega_0 t}], \end{aligned} \tag{6.65}$$

so that (6.58) (approach (b)) agrees with (6.40) (approach (a)). Both yield (6.41) or (see (6.51))

$$D_f(t) = -\Big\{H_\infty \omega_0^2 \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{\alpha_i\alpha_j(\alpha_i + i\omega_0)(\alpha_j + i\omega_0)}, 2\omega_0^2 \sum_{i=1}^{n} \frac{g_i}{\alpha_i^2 + \omega_0^2}\Big\}. \tag{6.66}$$

6.5.4. *Exponential history.* Using approach (b), we obtain from (6.59), (6.60) and (5.19) that

$$\begin{gathered}\psi_f(t) = \phi(t) + H_\infty \lambda^2 \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{\alpha_i\alpha_j(\alpha_i+\alpha_j)(\lambda+\alpha_i)(\lambda+\alpha_j)} E^2(t),\\ D_f(t) = H_\infty \lambda^2 \sum_{i,j=1}^{n} \frac{R_i^f R_j^f}{\alpha_i\alpha_j(\lambda+\alpha_i)(\lambda+\alpha_j)} E^2(t).\end{gathered} \tag{6.67}$$

Relation $(6.67)_1$ can be shown to agree with $(6.44)_1$, using minor modifications of the formulae showing the equivalence of the first parameter on the left of the brackets in (6.63) to that of (6.64). Relation $(6.67)_2$ clearly agrees with $(6.44)_2$ by virtue of (6.51) at $\omega = -i\lambda$.

6.6. **Proposed physical free energy.** A possible candidate for the true physical free energy, which is not uniquely identifiable for most materials with memory[2], was proposed in [17][3]. Expressions were given for general materials with only isolated singularities. If we restrict the singularities to be simple poles (discrete spectrum materials) this proposed free energy is given simply by the average of the ψ_f over all the factorizations labeled by f. A closed formula for this quantity was established, which can be put in the form

$$\psi_p(t) = \phi(t) + H_\infty \sum_{i,j=1}^{n} \frac{P(\alpha_i,\alpha_j)}{\alpha_i+\alpha_j} E_{r+}^t(-i\alpha_i) E_{r+}^t(-i\alpha_j), \tag{6.68}$$

where

$$P(\alpha_i,\alpha_j) = \frac{\alpha_i\alpha_j \prod_{k=2}^{n}\{\alpha_i\alpha_j + \gamma_k^2\}}{\prod_{\substack{k=1\\k\neq i}}^{n}(\alpha_i-\alpha_k)\prod_{\substack{k=1\\k\neq j}}^{n}(\alpha_j-\alpha_k)}. \tag{6.69}$$

Also, we have

$$D_p(t) == H_\infty \sum_{i,j=1}^{n} P(\alpha_i,\alpha_j) E_{r+}^t(-i\alpha_i) E_{r+}^t(-i\alpha_j). \tag{6.70}$$

This is the result from approach (b). There is no approach (a) since there is no result of this kind for a general relaxation function. Note that (6.68) and (6.70) correspond to (6.59) and (6.60) with $P(\alpha_i,\alpha_j)$ substituted for $R_i^f R_j^f$. We now give expressions for ψ_p and D_p for sinusoidal and exponential histories.

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[2] An exception is where $n = 1$ as observed in subsection 6.7.

[3] A valid question could be raised on whether a theoretical formula involving only the relaxation function parameters exists for all materials with memory. The other possibility could be that the physical rate of dissipation must be determined by measurement for each individual material and the associated free energy deduced from this [2].

6.6.1. *Sinusoidal histories.* Let us write (6.68) in the notation (5.13), using (5.10) and (6.11):

$$\begin{aligned}\psi_p(t) = \Big\{\frac{1}{2}G_\infty, G_\infty\Big\} + H_\infty\Big\{ &-\sum_{i,j=1}^{n} \frac{P(\alpha_i,\alpha_j)\omega_0^2}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i+i\omega_0)(\alpha_j+i\omega_0)},\\ &2\sum_{i,j=1}^{n} \frac{P(\alpha_i,\alpha_j)\omega_0^2(\alpha_i\alpha_j+\omega_0^2)}{(\alpha_i+\alpha_j)\alpha_i\alpha_j(\alpha_i^2+\omega_0^2)(\alpha_j^2+\omega_0^2)}\Big\}.\end{aligned} \tag{6.71}$$

Also,

$$D_p(t) = -\Big\{H_\infty\omega_0^2\sum_{i,j=1}^{n}\frac{P(\alpha_i,\alpha_j)}{\alpha_i\alpha_j(\alpha_i+i\omega_0)(\alpha_j+i\omega_0)}, 2\omega_0^2\sum_{i=1}^{n}\frac{g_i}{\alpha_i^2+\omega_0^2}\Big\}. \tag{6.72}$$

6.6.2. *Exponential history.* We obtain from (6.68) - (6.70) and (5.19) that

$$\begin{gathered}\psi_p(t) = \phi(t) + H_\infty\lambda^2\sum_{i,j=1}^{n}\frac{P(\alpha_i,\alpha_j)}{\alpha_i\alpha_j(\alpha_i+\alpha_j)(\lambda+\alpha_i)(\lambda+\alpha_j)}E^2(t),\\ D_f(t) = H_\infty\lambda^2\sum_{i,j=1}^{n}\frac{P(\alpha_i,\alpha_j)}{\alpha_i\alpha_j(\lambda+\alpha_i)(\lambda+\alpha_j)}E^2(t).\end{gathered} \tag{6.73}$$

6.7. **Day free energy.** Consider materials characterized by a relaxation function with only one decaying exponential, so that (4.1) and (4.3) become

$$G(t) = G_\infty + G_1e^{-\alpha t}, \quad G'(t) = ge^{-\alpha t}, \quad g = -\alpha G_1 < 0. \tag{6.74}$$

All free energies for such materials that are functionals of the minimal state reduce to the Day free energy functional [4], which is given by

$$\psi_{\rm Day}(t) = \phi(t) - \frac{\alpha g}{2}[E^t_{rL}(\alpha)]^2. \tag{6.75}$$

This can be shown for $\psi_{\rm Dill}$, ψ_F, ψ_f and ψ_p. It is not true for ψ_G and of course the work function. The corresponding rate of dissipation is

$$D_{\rm Day}(t) = -\alpha^2 g[E^t_{rL}(\alpha)]^2 = 2\alpha[\psi_{\rm Day}(t) - \phi(t)]. \tag{6.76}$$

The inequalities $(3.18)_1$ and (3.19) (or $(6.61)_1$, (6.62)) hold as equalities in this case.

For sinusoidal histories, we have from (5.10),

$$\begin{gathered}\psi_{\rm Day}(t) = \Big\{\frac{G_\infty}{2} + \frac{g\omega_0^2}{2\alpha}\frac{1}{(\alpha+i\omega_0)^2}, G_\infty - \frac{\omega_0^2}{\alpha}\frac{g}{\alpha^2+\omega_0^2}\Big\},\\ D_{\rm Day}(t) = \Big\{\frac{g\omega_0^2}{(\alpha+i\omega_0)^2}, -2\frac{\omega_0^2 g}{\alpha^2+\omega_0^2}\Big\},\end{gathered} \tag{6.77}$$

while for exponential histories, (5.19) (or remark 5.1) yields

$$\psi_{\rm Day}(t) = \frac{1}{2}\big[G_\infty - \frac{g}{\alpha}\frac{\lambda^2}{(\lambda+\alpha)^2}\big]E^2(t), \quad D_{\rm Day}(t) = -\frac{g\lambda^2}{(\lambda+\alpha)^2}E^2(t). \tag{6.78}$$

Let us present the form of the Graffi-Volterra function and the work function for relaxation functions with a single exponential. The former and its rate of dissipation are given by a special case of (6.5):

$$\psi_G(t) = \phi(t) - \frac{1}{2}gE^t_{sLr}(\alpha), \quad D_G(t) = -\frac{1}{2}\alpha gE^t_{sLr}(\alpha) = \alpha[\psi_G(t) - \phi(t)], \tag{6.79}$$

where E^t_{sLr} is defined by (6.6). These become for sinusoidal histories, by (6.12),

$$\begin{gathered}\psi_G(t) = \Big\{\frac{1}{2}G_\infty - \frac{g}{2}\big[\frac{1}{\alpha+2i\omega_0} - \frac{2}{\alpha+i\omega_0} + \frac{1}{\alpha}\big], G_\infty - 2g\big[\frac{1}{\alpha} - \frac{\alpha}{\alpha^2+\omega_0^2}\big]\Big\} \\ D_G(t) = -g\Big\{\frac{\alpha}{2}\big[\frac{1}{\alpha+2i\omega_0} - \frac{2}{\alpha+i\omega_0} + \frac{1}{\alpha}\big], \frac{2\omega_0^2}{\alpha^2+\omega_0^2}\Big\}.\end{gathered} \tag{6.80}$$

For exponential histories

$$\begin{gathered}\psi_G(t) = \frac{1}{2}\Big[G_\infty - g\Big(\frac{1}{\alpha+2\lambda} - \frac{2}{\alpha+\lambda} + \frac{1}{\alpha}\Big)\Big]E^2(t), \\ D_G(t) = -\frac{g\alpha}{2}\Big(\frac{1}{\alpha+2\lambda} - \frac{2}{\alpha+\lambda} + \frac{1}{\alpha}\Big)E^2(t).\end{gathered} \tag{6.81}$$

We can write the work function for one exponential using (3.1) and (4.6) but the resulting expression, though general, is not particularly useful. For sinusoidal histories however, we can use (6.2) to write

$$W(t) = \Big\{\frac{1}{2}\big[G_0 + \frac{g}{\alpha+i\omega_0}\big], G_0 + \frac{\alpha g}{\alpha^2+\omega_0^2} + \frac{2\omega_0^2\alpha g}{(\alpha^2+\omega_0^2)^2} - \frac{\omega_0^2 g}{\alpha^2+\omega_0^2}\big(2t + \frac{1}{\eta}\big)\Big\}. \tag{6.82}$$

Also, we can use (6.4) in the case of exponential histories to write

$$W(t) = \frac{1}{2}\big[G_0 + \frac{g}{\alpha+\lambda}\big]E^2(t). \tag{6.83}$$

Remark 6.3. In the case of materials for which the relaxation function is well approximated by one decaying exponential, there is a strong argument for identifying $\psi_{\rm Day}$ as the physical free energy.

7. Choices of decay constant

Our choice of inverse decay times α_i, $i = 1, 2, \dots, n$, will be based on classical theoretical arguments. We shall adopt the following formula, which emerges from simple Brownian motion molecular theories (see references in [13] and [15] for example):

$$\alpha_r = \alpha_n\kappa_r, \quad \kappa_r = \frac{\sin^2[\frac{r\pi}{2(n+1)}]}{\sin^2[\frac{n\pi}{2(n+1)}]}, \quad r = 1, 2, \dots, n. \tag{7.1}$$

The quantity κ_1 as a function of n is plotted on figure 1. This and all other graphical output was produced on Matlab 7.0.1.

For most of the plots presented, we take $n = 4$. This relatively low value is adopted because, as noted in remark 3.1, the approach from a discrete to a continuous spectrum occurs remarkably quickly as n increases, at least according to one particular measure, namely that given by (3.32).

The coefficients G_i in (4.1) are all taken to be the same [13]:

$$G_i = G_1, \quad i = 1, 2, \dots, n. \tag{7.2}$$

We assume that E_0 in (5.4) is real, so that

$$E(t) = 2E_0\cos\omega_0 t. \tag{7.3}$$

Dimensions will be removed from the expressions, by taking all free energies as divided by $G_0E_0^2$, for sinusoidal histories and by $G_0E_1^2$ for exponential histories. In the case of the rate of dissipation associated with a given free energy, we divide

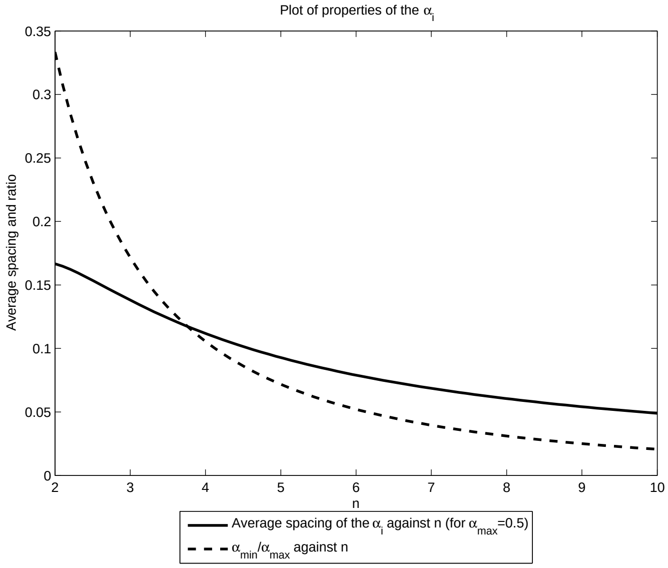

FIGURE 1. Average spacing between the α_i against n. Also, the ratio $\alpha_{\min}/\alpha_{\max}$ against n

by $G_0E_0^2\omega_0$ for sinusoidal histories and by $G_0E_1^2\lambda$ for exponential histories. These procedures amount to taking

$$G_0 = E_0 = E_1 = 1, \tag{7.4}$$

which is henceforth assumed in the numerical work. Apart from time and the value of n, the remaining parameters are $\alpha_m = \alpha_{\max}$ and G_∞ (G_∞/G_0 in dimensionless coordinates which varies in $[0,1]$). Observe that, by virtue of (4.3), the quantity G_1 in (7.2) is then given uniquely by

$$G_1 = \frac{1}{n}[1 - G_\infty] \in [0, \frac{1}{n}]. \tag{7.5}$$

Suitable dimensionless variables must be selected for both types of strain histories. For sinusoidal histories, we choose

$$\rho = \frac{\alpha_n}{\omega_0}, \quad \tau = \omega_0 t \tag{7.6}$$

as our remaining dimensionless quantities characterizing the material behaviour. The latter is in effect a dimensionless time variable. For exponential histories, the corresponding choices are

$$\rho = \frac{\alpha_n}{\lambda}, \quad \tau = \lambda t. \tag{7.7}$$

Relations (7.6) and (7.7) are equivalent to taking

$$\omega_0 = \lambda = 1. \tag{7.8}$$

Remark 7.1. In some of the plots presented, we deal with measures of free energy and rate of dissipation that are independent of time. In the case of sinusoidal histories, the natural quantities are the averages of the functional over a cycle, or N in (5.12) (divided by $G_0E_0^2$ for free energies and $G_0E_0^2\omega_0$ for dissipation rates, as observed earlier). For exponential histories, it is $\psi(t)/(G_0E^2(t))$ for free energies and $\psi(t)/(G_0E^2(t)\lambda)$ for rates of dissipation.

The algebraic expressions in these two cases are quite different. For example, the expression $\psi(t)/(G_0E^2(t))$ has a close relation to the corresponding choice of M in (5.12) (through analytic continuation; see remark 5.1) but not N.

8. Discussion of results

Various numerical plots are presented on figure 2 - 21 in the appendix. On figures 2 - 9, free energies and rates of dissipation are plotted against time. On figures 2 and 6, the minimum, maximum and two of the intermediate free energies discussed in subsections 3.5 and 6.5 are shown for sinusoidal and exponential histories with $n = 4$. Note that in the case of exponential histories, the time dependence is a trivial factor $E^2(t)$. The interesting information is contained in the factor multiplying this quantity, which we will explore in more detail below. Because of this, we have chosen a very short time interval which yields good separation between the different curves.

The work function is included for exponential histories but not in the case of sinusoidal histories, for which it is divergent.

The main information content on both sets of curves is the vertical ordering of the free energies. In particular, the close proximity (figures 4, 8) of the minimum free energy $\psi_m(t)$ and $\psi_F(t)$ is noteworthy. They appear to be almost equal. The difference for the rates of dissipation (figures 5, 9) is slightly larger. There is no apparent algebraic evidence for equality. The quantity $\psi_m(t)$ can be expressed as a quadratic form in the quantity $\dot{I}^t(s)$ given by (3.20) [8, 2], but the kernel is quite different from that in (3.20). The almost equally close correspondence between $\psi_{\rm Dill}(t)$ and $\psi_m(t)$, $\psi_F(t)$ is also interesting. This feature does not appear to be a consequence of the special assumptions made in section 7, in particular (7.2). Even when this is altered, the close proximity of these quantities is retained. This phenomenon will be discussed further below.

The somewhat central position of $\psi_p(t)$ is to be expected. In figure 4, $\psi_G(t)$ crosses over the curve for $\psi_M(t)$, which is consistent with the observation just before remark 3.1.

The behaviour of the rates of dissipation on figure 3 are in agreement with the features listed in remarks 6.1 and 6.2, including those for the maximum free energy. Note that, on figures 3 and 5, the maximum free energy is out of phase with the minimum free energy by around $\pi/2$. This, however, is not a general feature.

The ordering noted in the last paragraph of remark 2.1 is reflected in figures 7 and 9. We observe that on figure 8, the maximum free energy is very close to the work function, even for $n = 4$.

On figures 10 - 12, the effects of varying $\alpha_{\max}$ on free energies and dissipation rate are presented for sinusoidal histories, while on figures 13 - 16, similar data are plotted for exponential histories. For sinusoidal histories, there is only one average dissipation rate, as observed after (6.10).

The proximity of the minimum free energy, ψ_F and $\psi_{\rm Dill}$ is evident on all these plots, though the separation is slightly more apparent on figure 16. One might therefore tentatively make the hypothesis that the phenomenon is present for all histories and is worthy of further exploration. Let us briefly discuss the issue using a different approach that applies to all histories, though for fixed values of $\alpha_{\max}$

and G_∞. This approach turns out to provide interesting insights, but again is not finally conclusive with regard to general histories.

It is noted in [2] and references cited therein that all free energies that are functionals of the minimal state for discrete spectrum materials can be expressed in the form

$$\psi(t)=\phi(t)+\frac{1}{2}\mathbf{e}^\top\mathbf{C}\mathbf{e}=\phi(t)+\frac{1}{2}\mathbf{e}\cdot\mathbf{C}\mathbf{e}, \tag{8.1}$$

where $\mathbf{e}$ is a vector in $\mathbb{R}^n$ with components

$$\begin{aligned} e_i(t)&=E(t)-\alpha_i E_+^t(-i\alpha_i)=\frac{d}{dt}E_+^t(-i\alpha_i)\\ &=-\alpha_i E_{r+}^t(-i\alpha_i),\quad i=1,2,\dots,n. \end{aligned} \tag{8.2}$$

and $\mathbf{C}$ is a symmetric, positive definite matrix of components C_{ij}, $i,j=1,2,\dots,n$. It has the property that

$$\sum_{j=1}^n C_{ij}=G_i,\quad i=1,2,\dots,n, \tag{8.3}$$

where the coefficients G_i are those in (4.1). Also, the rate of dissipation is given by

$$D(t)=\frac{1}{2}\mathbf{e}^\top\boldsymbol{\Gamma}\mathbf{e},\quad \Gamma_{ij}=(\alpha_i+\alpha_j)C_{ij}, \tag{8.4}$$

where Γ_{ij} $i,j=1,2,\dots,n$ are the elements of the matrix $\boldsymbol{\Gamma}$ which must be at least positive semi-definite.

Relation (6.59) yields explicit forms for $\mathbf{C}$ and $\boldsymbol{\Gamma}$ corresponding to the minimum and related free energies given by

$$C_{ij}^f=2H_\infty\frac{R_i^fR_j^f}{(\alpha_i+\alpha_j)\alpha_i\alpha_j},\quad \Gamma_{ij}^f=2H_\infty\frac{R_i^fR_j^f}{\alpha_i\alpha_j}. \tag{8.5}$$

In the case of ψ_p, we have

$$C_{pij}=2H_\infty\frac{P(\alpha_i,\alpha_j)}{(\alpha_i+\alpha_j)\alpha_i\alpha_j},\quad \Gamma_{pij}=2H_\infty\frac{P(\alpha_i,\alpha_j)}{\alpha_i\alpha_j}, \tag{8.6}$$

where P is given by (6.69). For the Dill free energy, $\mathbf{C}$ and Γ are diagonal. We have

$$C_{Dij}=\Gamma_{Dij}=0,\quad i\neq j,\quad C_{Dii}=-\frac{g_i}{\alpha_i},\quad \Gamma_{Dii}=-2g_i. \tag{8.7}$$

For ψ_F we have

$$C_{Fij}=-\int_0^\infty\frac{g_ig_je^{(\alpha_i+\alpha_j)\tau}}{\sum_{l=1}^n g_le^{-\alpha_l\tau}}d\tau,\quad \Gamma_{Fij}=(\alpha_i+\alpha_j)C_{Fij} \tag{8.8}$$

Consider relation (8.1) in diagonal form. Let $\mathbf{d}=\mathbf{R}^\top\mathbf{e}$ where $\mathbf{R}$ is the rotation matrix such that $\mathbf{R}^\top\mathbf{C}\mathbf{R}$ is a diagonal matrix. Then, (8.1) becomes

$$\psi(t)=\phi(t)+\frac{1}{2}\sum_{i=1}^n\beta_id_i^2, \tag{8.9}$$

where d_i are the components of $\mathbf{d}$ and β_i are the eigenvalues of $\mathbf{C}$.

We take $n=4$, so that $\mathbf{C}_f$ includes $\mathbf{C}_m,\mathbf{C}_{int1},\mathbf{C}_{int2}$ and $\mathbf{C}_M$ where $\mathbf{C}_{int1}$ and $\mathbf{C}_{int2}$ refer to two intermediate free energies (see subsection 3.5). Also, let us choose $\alpha_{\max}=0.5$ and $G_\infty=0.1$ as in several of the figures.

Table 1. Eigenvalues and the vectors $\mathbf{d}$ for each free energy and difference between free energies.

$\mathbf{C}$	$\beta_i, \quad i = 1,2,3,4$	$d_i^2, \quad i = 1,2,3,4$
$\mathbf{C}_m$	5.2E-5, 2.5E-3, 3.6E-2, 2.2E-1	1.1E-3, 2.2E-2, 7.1E-2, 13.3
$\mathbf{C}_{\text{int1}}$	1.4E-4, 1.2E-2, 2.3E-1, 1.9	2.9E-3, 6.6E-2, 13.3, 2.5E-2
$\mathbf{C}_{\text{int2}}$	2.5E-3, 2.25E-1, 1.5, 29.2	2.7E-2, 13.3, 5.5E-2, 1.1E-2
$\mathbf{C}_p$	2.25E-1, 1.1, 9.9, 175	13.3, 6.6E-2, 2.6E-2, 1.7E-3
$\mathbf{C}_M$	2.25E-1, 1.4, 20.5, 970	13.3, 7.1E-2, 2.2E-2, 1.1E-3
$\mathbf{C}_D$	2.2E-1, 2.2E-1, 2.2E-1, 2.2E-1	3.1, 3.7, 4.0, 2.6
$\mathbf{C}_F$	3.3E-4, 1.1E-2, 9.9E-2, 2.2E-1	2.1E-3, 2.8E-2, 6.4E-2, 13.3
$\mathbf{C} - \mathbf{C}_m$	$\beta_i, \quad i = 1,2,3,4$	$d_i^2, \quad i = 1,2,3,4$
$\mathbf{C}_{int1} - \mathbf{C}_m$	0.0, 0.0, 0.0, 1.8	11.2, 9.3E-1, 1.2, 2.4E-2
$\mathbf{C}_{int2} - \mathbf{C}_m$	0.0, 0.0, 1.4, 29.2	3.0, 10.3, 5.5E-2, 1.1E-2
$\mathbf{C}_p - \mathbf{C}_m$	0.0, 1.1, 9.9, 172	13.3, 6.6E-2, 2.6E-2, 1.7E-3
$\mathbf{C}_M - \mathbf{C}_m$	0.0, 1.4, 20.5, 970	13.3, 7.1E-2, 2.2E-2, 1.1E-3
$\mathbf{C}_F - \mathbf{C}_m$	6.3E-2, 8.6E-3, 1.6E-8, 2.6E-4	5.9E-2, 3.2E-2, 13.3, 2.6E-3
$\mathbf{C}_D - \mathbf{C}_m$	0.0, 1.9E-1, 2.2E-1, 2.2E-1	13.3, 7.1E-2, 2.2E-2, 1.1E-3

It follows from (8.1) that

$$\psi(t) - \psi_m(t) = \frac{1}{2}\mathbf{e} \cdot [\mathbf{C} - \mathbf{C}_m]\,\mathbf{e}, \tag{8.10}$$

where $\psi(t)$ is any one of the others free energies considered above. This relation can be expressed in diagonal form, as in the case of (8.9), yielding

$$\psi(t) - \psi_m(t) = \frac{1}{2}\sum_{i=1}^{n} \beta_i d_i^2, \tag{8.11}$$

where d_i and β_i are defined as before but in relation to the matrices $[\mathbf{C} - \mathbf{C}_m]$.

On table 1, the eigenvalues of the various matrices $\mathbf{C}$ and the differences $[\mathbf{C} - \mathbf{C}_m]$ are presented with the corresponding vectors $\mathbf{d}$. These latter quantities are calculated for sinusoidal histories, as given by (5.10), for $t = 0$. Note that the eigenvalues are intrinsic properties of the matrices involved, for specified values of $\alpha_{\max}$ and G_∞, which are independent of the history chosen, while the vectors $\mathbf{d}$ relate to a particular history, chosen for illustrative purposes to be sinusoidal.

All the eigenvalues on table 1 are positive, which is consistent with the fact that all the matrices involved are positive. Those eigenvalues indicated as zero on the second part of the table are in fact very small positive numbers in the region $10^{-14} - 10^{-18}$, which clearly cannot be stated with any accuracy. Thus, $\mathbf{C}_m$, $\mathbf{C}_{int1}$, $\mathbf{C}_F$ and several of the differences in the lower part of the table are positive definite but very close to being positive semi-definite.

In the top part of the table, the eigenvalues of the various matrices are consistent with the ordering indicated by the plots. Strictly, however, one cannot deduce that this must be the case in general because the d_i^2 will be different in most cases.

Regarding the proximity of ψ_m and ψ_F, we see that the dominant terms in both cases are $13.3 \times 2.2E - 1$, while the other terms are negligible in comparison. However, because we include the d_i^2, this comparison refers to sinusoidal histories, for which the graphical data already clearly shows that the two quantities are very close. A more general argument, independent of the history chosen, is that the eigenvalues of $\mathbf{C}_F - \mathbf{C}_m$ are all very small. This is not quite conclusive in general in that we see from (8.11) that if one or more of the d_i^2 for a particular history are large, then this could perhaps compensate. However, the d_i are constrained by the requirement that $\mathbf{d} \cdot \mathbf{d} = \mathbf{e} \cdot \mathbf{e}$.

Somewhat similar arguments apply to $\mathbf{C}_{int1}$ and $\mathbf{C}_m$, which are indeed close on the plots for some sinusoidal histories though not so markedly for others and for exponential histories.

Also, it is clear that $\mathbf{C}_D - \mathbf{C}_m$ has reasonably small eigenvalues. We deduce from $(4.3)_2$, (4.6) and (6.52) that, for purposes of determining asymptotic behaviour, the R_i^f can be treated as linear in the inverse decay times α_k, $k = 1, 2, \dots, n$.

It is clear both from figures 10, 11 and the formulae in section 6 that, at small values of $\alpha_{\max}$, all the averages of the free energy functionals (over cycles) approach G_0 except for the Graffi-Volterra functional which tends to $2G_0 - G_\infty$ (figure 11 and (6.8)). This is connected with the fact that $\psi_G(t)$ exceeds $\psi_M(t)$ for smaller values of $\alpha_{\max}$. We refer again here to the comment before remark 3.1.

The magnitudes of free energies tend to decrease as $\alpha_{\max}$ increases, though for larger $\psi(t)$, there is an increase followed by a decrease. They do not go to zero at large $\alpha_{\max}$, which can be confirmed from the relevant formulae in section 6. The hump-shaped curve for the rate of dissipation, shown on figure 12, is simply related to the loss modulus $|G_s'(\omega_0)|$. Its maximum is just above unity. It tends to zero, slowly, at large $\alpha_{\max}$.

For exponential histories (figures 13 - 16) all free energies decline in magnitude for increasing $\alpha_{\max}$. All free energy functionals approach $0.5G_0$ (figures 13 and 15) at small $\alpha_{\max}$. Also, on figures 14 and 16 for rates of dissipation, the hump-shaped curves are again manifest, with maxima at positions that increase as the maximum values increase. The rates of dissipation approach zero in all cases as $\alpha_{\max}$ tends to zero. This is clear from the formulae in section 6 and figures 14, 16. They fall to zero at large $\alpha_{\max}$, though slowly in some cases.

If G_∞ is varied, keeping $\alpha_{\max}$ fixed, the plots are simple straight lines for the model considered in this section. These are omitted, though we now show how they can be determined from existing data.

For sinusoidal histories, we see from section 6 that all the average free energies can be written as

$$\frac{\langle \psi(t) \rangle_{av}}{|E_0|^2} = 1 + m_\psi(\alpha_i) G_1, \tag{8.12}$$

where G_1 is given by (7.5). This quantity is more convenient than G_∞ for present purposes. For the dimensionless version of the theory, we have from (7.4) that $G_0 = 1$. In deducing (8.12) for free energies given by (6.63), it is important to note that, because (7.2) applies, the zeros γ_i^2, defined after (4.7), depend only on the α_i and not on the coefficients g_i in (4.3). The values of $\langle \psi(t) \rangle_{av}$ plotted on figures 10, 11 are for $G_1 = 0.225$. It follows that the slope $m(\alpha_i)$ is given by

$$m_\psi(\alpha_i) = \frac{1}{0.225} \Big[\frac{\langle \psi(t) \rangle_{av}}{G_0 |E_0|^2} - 1 \Big]. \tag{8.13}$$

From sample calculations (or figures 10, 11), it emerges that this quantity is negative for smaller free energies, in particular the minimum free energy, and positive for larger choices, notably the maximum free energy. Similarly, the average rate of dissipation is given in all cases by

$$\frac{\langle D(t)\rangle_{av}}{G_0|E_0|^2\omega_0} = m_D(\alpha_i)G_1, \tag{8.14}$$

where the slope $m_D(\alpha_i)$ can be deduced for any of the values of $\frac{\langle D(t)\rangle_{av}}{G_0|E_0|^2\omega_0}$ shown on figure 12 to be

$$m_D(\alpha_i) = \frac{1}{0.225}\frac{\langle D(t)\rangle_{av}}{G_0|E_0|^2\omega_0}. \tag{8.15}$$

Note that $m_D(\alpha_i) \geq 0$, which relates to the fact that as G_1 increases (or G_∞ decreases) the internal dissipation in the material increases.

Corresponding observations apply to the free energies and rates of dissipation given in section 6 for exponential histories. Notable differences from the above discussion are that G_0 is replaced by $G_0/2$ (that is, the intercept becomes 0.5) in (8.12) and the slope m_ψ is always negative, by virtue of figures 13, 15.

The Graffi-Volterra free energy for $n = 1$, the Day free energy and, in the case of exponential histories, the work function for $n = 1$ are presented on figures 17 - 20. We see that the Graffi-Volterra free energy exceeds the Day free energy for both histories. For exponential histories, the dissipation rate is less for the Graffi-Volterra case than for the Day case, in accordance with remark 2.1.

On figure 21, we explore, for exponential histories, the approach of $\psi_M(t)$ to $W(t)$ as n increases, or (see figure 1) as the average spacing between the α_i decreases. The quantity R_ψ of (2.9) is plotted. From figure 19, it is clear that for $n = 1$, this ratio is about 0.7 for $\alpha = 0.5$ and $G_\infty = 0.1$. If $n = 3$, the ratio has increased to in excess of 0.98 for all the values shown. For higher values of n, the ratios are in excess of 0.99, so the approach is very rapid.

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REFERENCES

[1] G. Amendola, M. Fabrizio, J. M. Golden; *Free energies in a general non-local theory of a material with memory*, Models and Methods in Applied Sciences 24 (2014), 1037-1090.

[2] G. Amendola, M. Fabrizio, M. Golden; *Thermodynamics of Materials with Memory: Theory and Applications*, Springer, New York, 2012.

[3] B. D. Coleman; *Thermodynamics of materials with memory*, Arch. Rational Mech. Anal. **17** (1964), 1-45.

[4] W. A. Day; *The thermodynamics of materials with memory*, in *Materials with Memory*, ed. D. Graffi, Liguori, Naples, 1979.

[5] G. Del Piero, L. Deseri; *On the analytic expression of the free energy in linear viscoelasticity*, J. Elasticity **43** (1996), 247-278.

[6] G. Del Piero, L. Deseri; *On the concepts of state and free energy in linear viscoelasticity*, Arch. Rational Mech. Anal. **138** (1997), 1-35.

[7] L. Deseri, G. Gentili, J. M. Golden; *An explicit formula for the minimum free energy in linear viscoelasticity*, J. Elasticity **54** (1999), 141-185.

[8] L. Deseri, M. Fabrizio, J. M. Golden; *On the concept of a minimal state in viscoelasticity: new free energies and applications to* PDE_S, Arch. Rational Mech. Anal. **181** (1) (2006), 43-96.

[9] L. Deseri, J. M. Golden; *The minimum free energy for continuous spectrum materials*, SIAM J. Appl Math. **67** (2007), 869-892.

[10] M. Fabrizio, A. Morro; *Mathematical Problems in Linear Viscoelasticity*, SIAM, Philadelphia, 1992.

[11] M. Fabrizio, J. M. Golden; *Maximum and minimum free energies for a linear viscoelastic material*, Quart. Appl. Math. **60** (2002), 341-381.

[12] M. Fabrizio, G. Gentili, J. M. Golden; *Free energies for linear non-isothermal materials with memory*, Mathematical and Computer Modelling **39** (2004), 219-253.

[13] J. D. Ferry; *Viscoelastic Properties of Polymers*, 3rd edn, John Wiley, New York, 1980.

[14] G. Gentili; *Maximum recoverable work, minimum free energy and state space in linear viscoelasticity*, Quart. Appl. Math. **60** (2002), 153-182.

[15] J. M. Golden; *A molecular theory of adhesive rubber friction*, J. Phys. A **39** (2001) 53-70.

[16] J. M. Golden; *Free energies in the frequency domain: the scalar case*, Quart. Appl. Math. **58** (2000), 127-150.

[17] J. M. Golden; *A proposal concerning the physical rate of dissipation in materials with memory*, Quart. Appl. Math. **63** (2005), 117-155.

[18] J. M. Golden; *A proposal concerning the physical rate of dissipation of materials with memory: the non-isothermal case*, Mathematics and Mechanics of Solids **12** (4) (2007), 403-449.

[19] D. Graffi; *Sull'expressione analitica di alcune grandezze termodinamiche nei materiali con memoria*, Rend. Sem. Mat. Univ. Padova **68** (1982), 17-29.

[20] D. Graffi, M. Fabrizio; *Sulla nozione di stato materiali viscoelastici di tipo 'rate'*, Atti della Accademia Nazionale dei Lincei **83** (1990), 201-208.

[21] D. Graffi; *Ancora sull'expressione analitica dell'energia libera nei materiali con memoria*, Atti Acc. Scienze Torino **120** (1986), 111-124.

[22] W. Noll; *A new mathematical theory of simple materials*, Arch. Rational Mech. Anal. **48** (1972), 1-50.

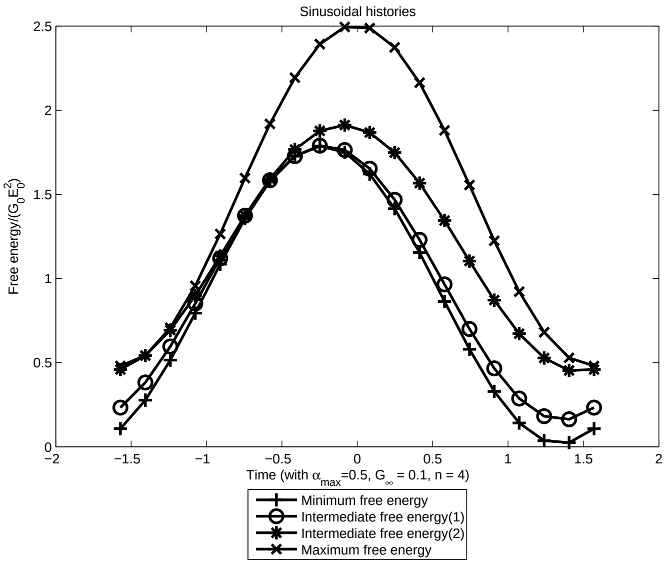

FIGURE 2. Minimum, maximum and intermediate free energies

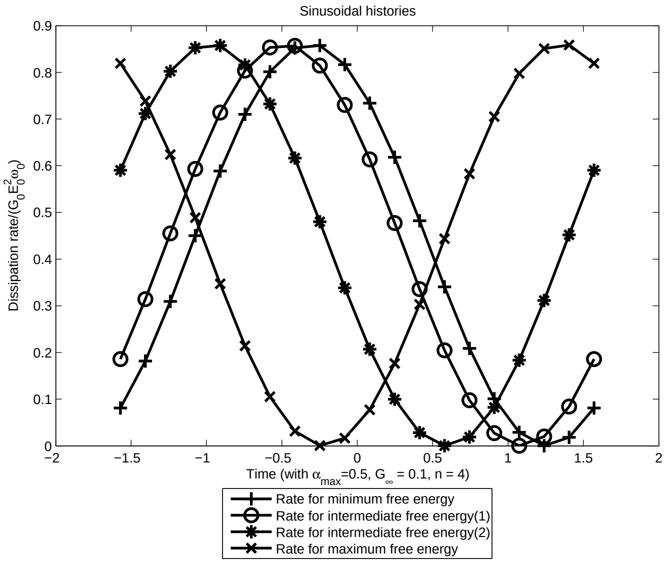

FIGURE 3. Rates of dissipation relating to the free energies on figure 2

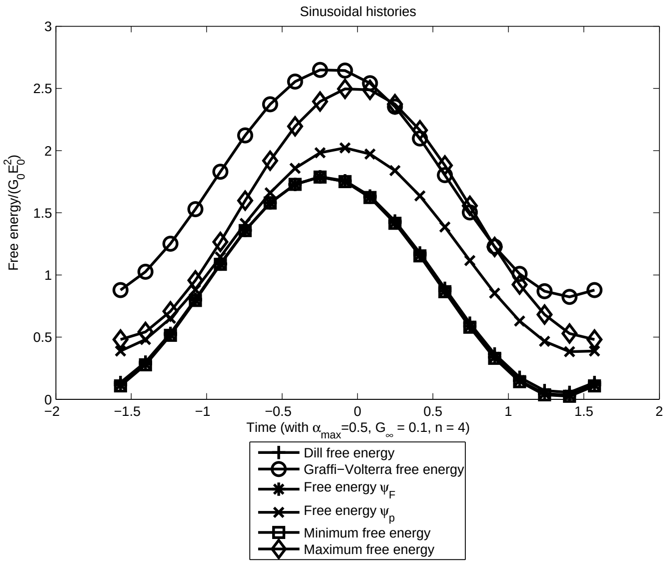

FIGURE 4. Free energies as listed

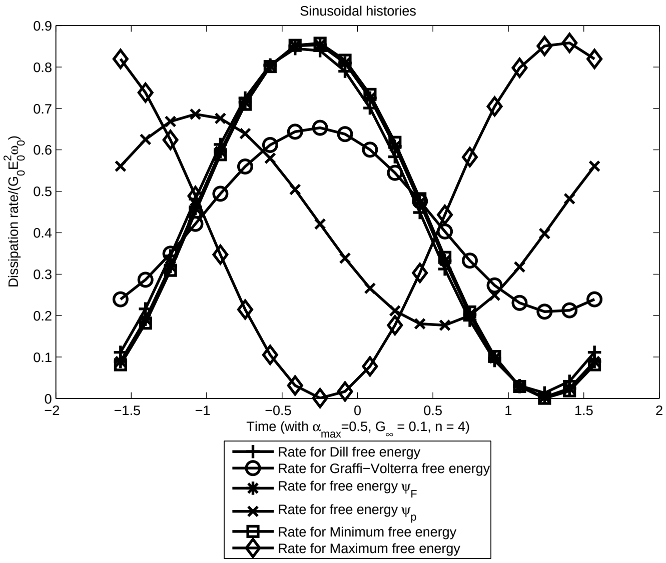

FIGURE 5. Rates of dissipation relating to the free energies on figure 4

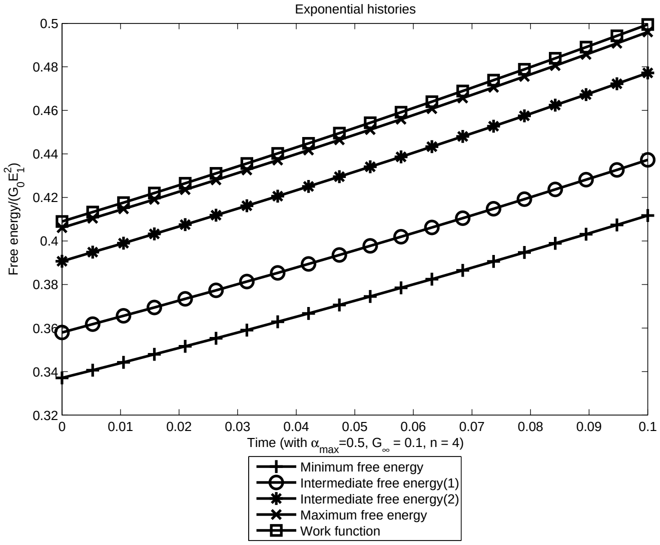

FIGURE 6. Minimum, maximum and intermediate free energies

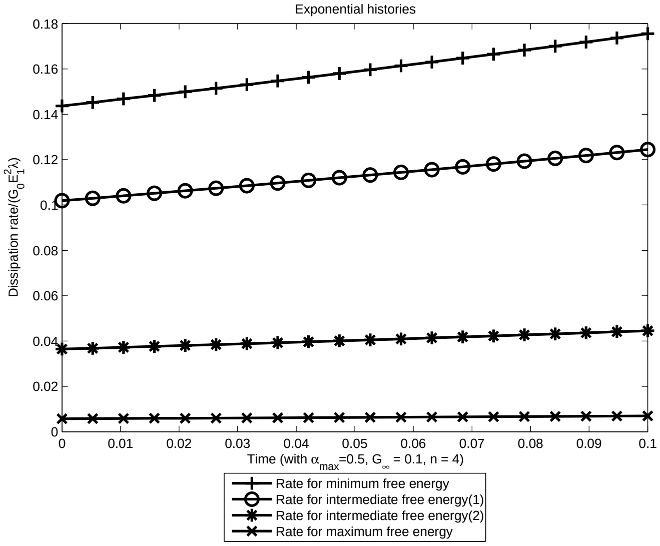

FIGURE 7. Rates of dissipation relating to the free energies on figure 6

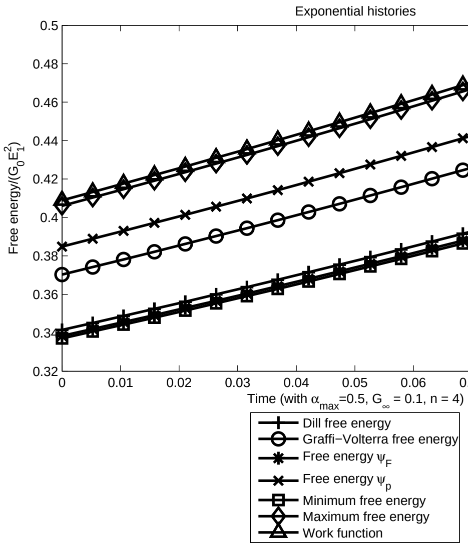

FIGURE 8. Free energies as listed

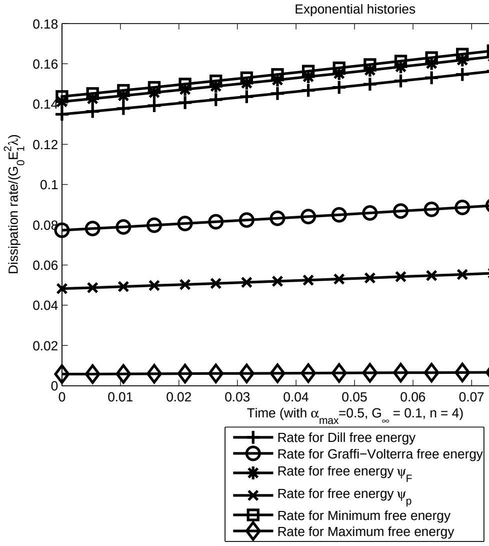

FIGURE 9. Rates of dissipation relating to the free energies on figure 8

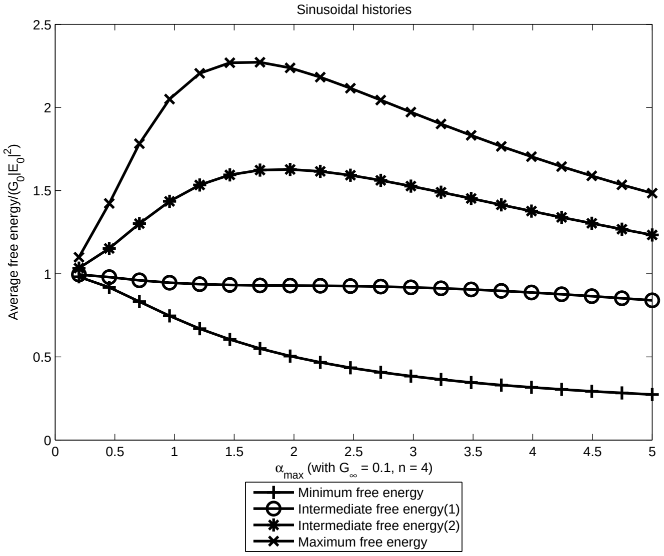

FIGURE 10. Minimum, maximum and intermediate free energies

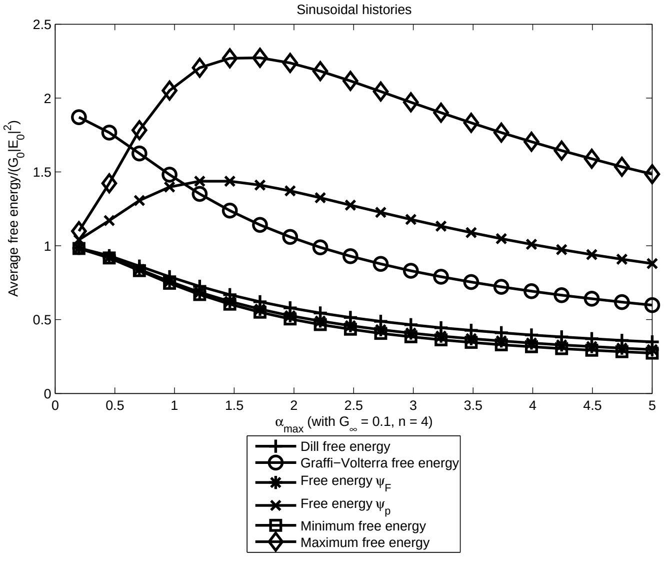

FIGURE 11. Free energies as listed

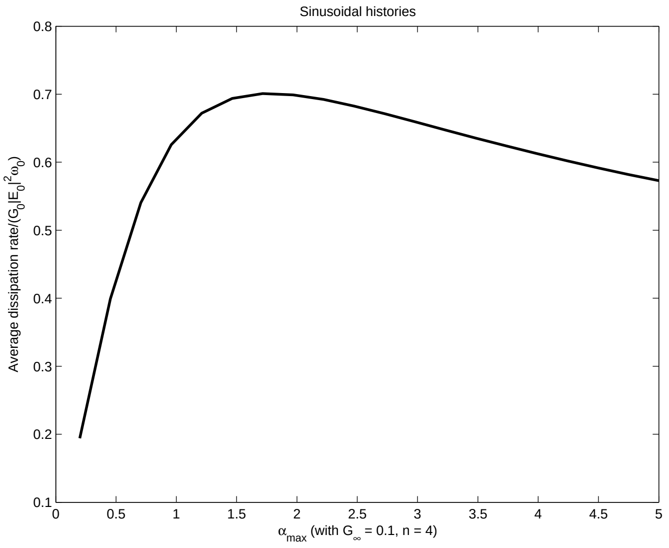

Figure 12. Rate of dissipation relating to all free energies

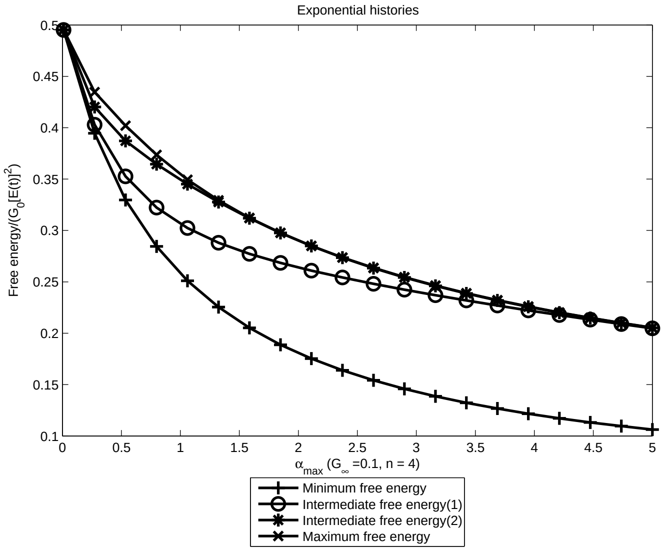

Figure 13. Minimum, maximum and intermediate free energies

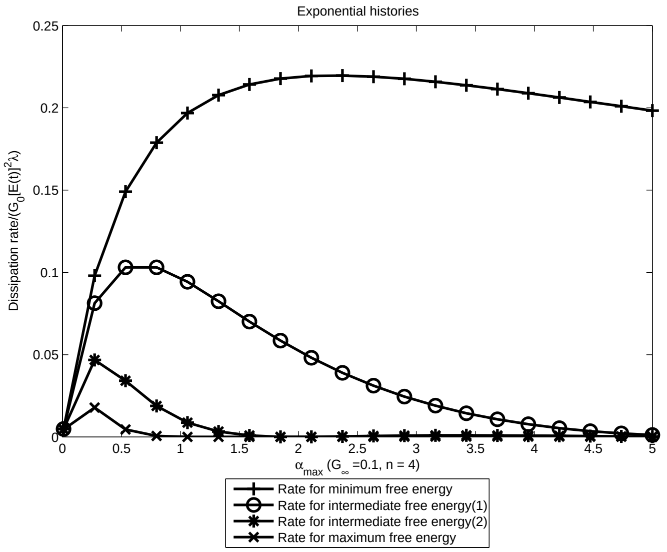

Figure 14. Rates of dissipation relating to the free energies on figure 13

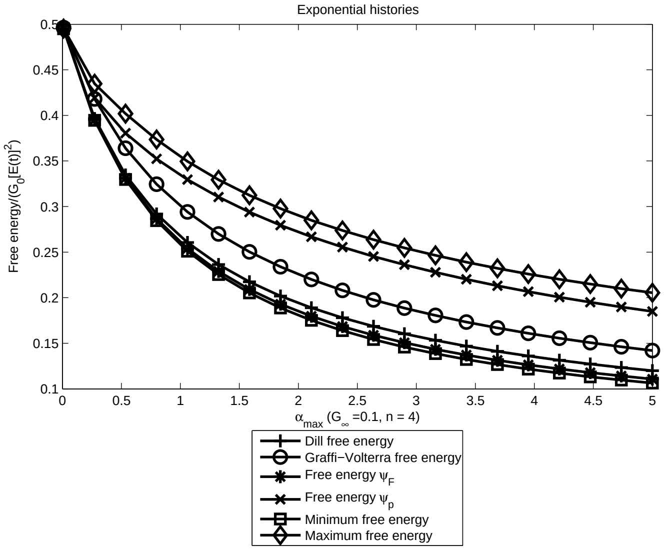

Figure 15. Free energies as listed

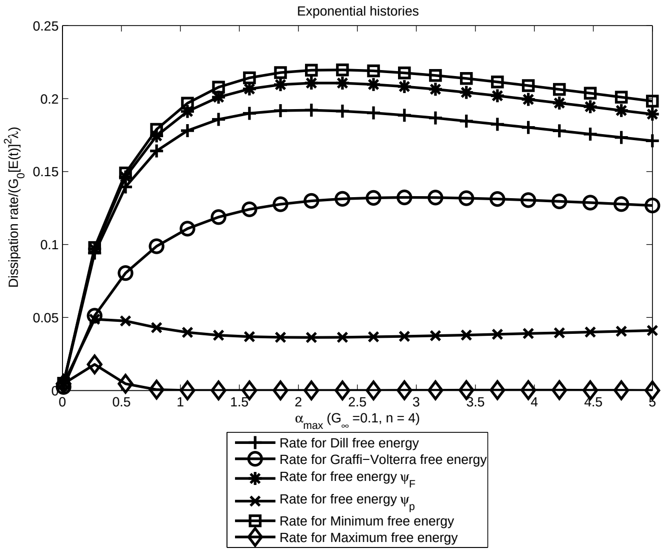

FIGURE 16. Rates of dissipation relating to the free energies on figure 15

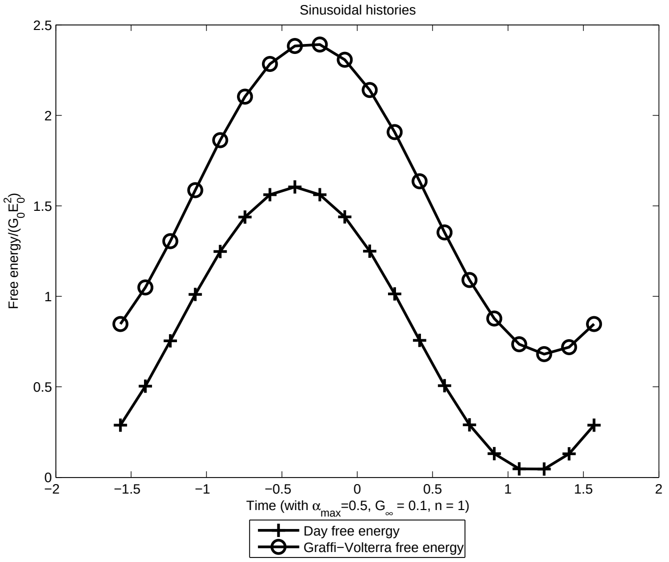

FIGURE 17. Day and Graffi-Volterra free energies (n=1)

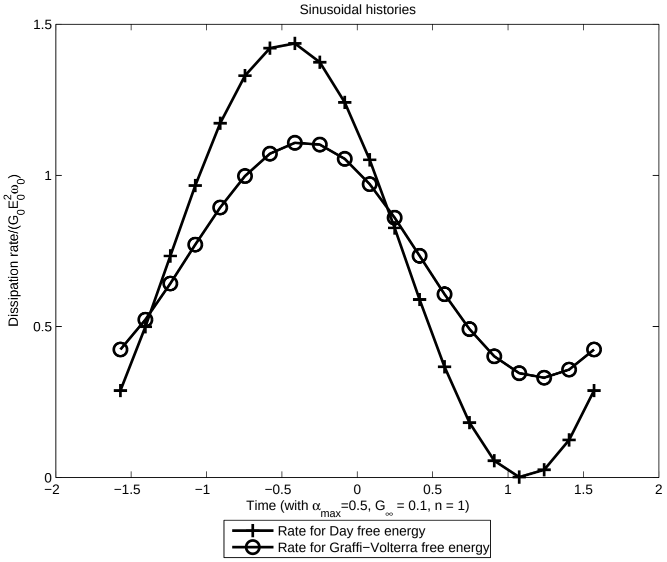

Figure 18. Day and Graffi-Volterra dissipation rates

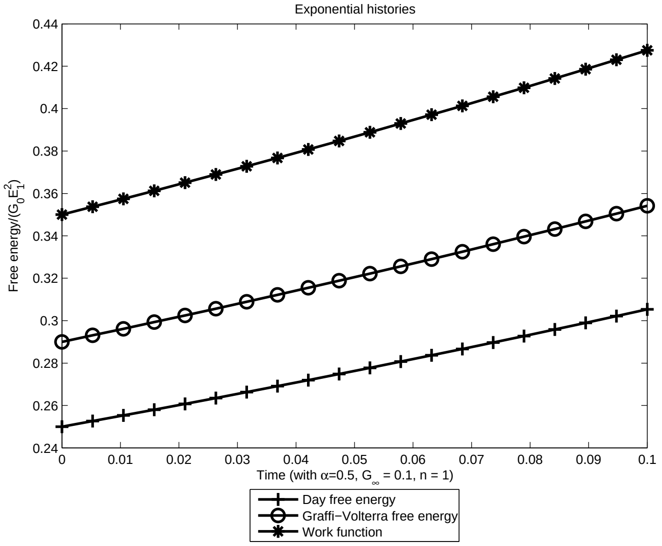

Figure 19. Day and Graffi-Volterra free energies

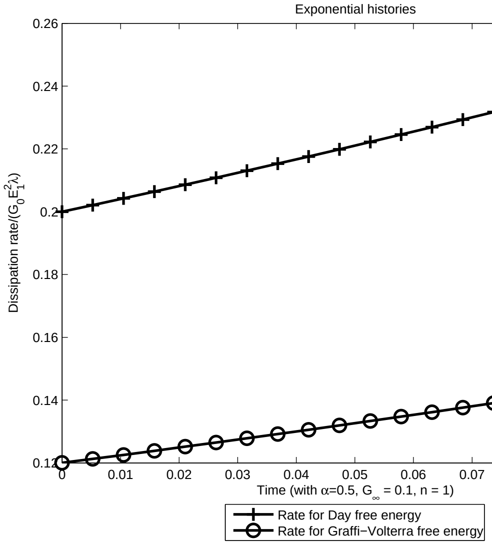

FIGURE 20. Day and Graffi-Volterra dissipation rates

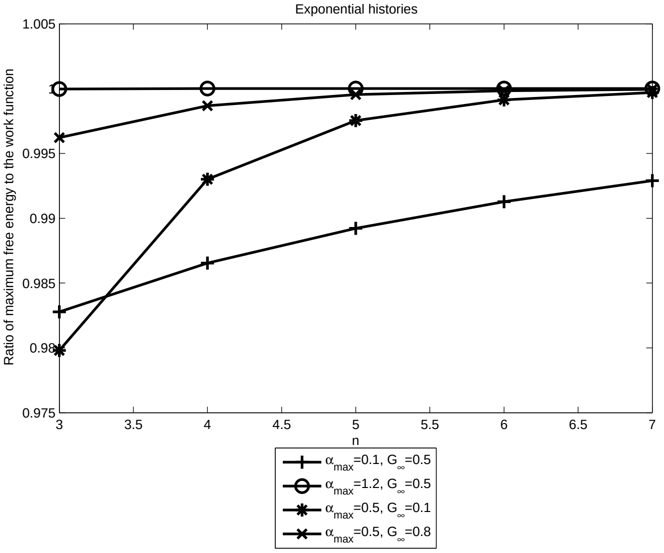

FIGURE 21. Approach of ψ_M to the work function $W(t)$

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