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Dielectric Materials with Memory II: Free Energies in Non-Magnetic Materials

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Abstract

An isothermal theory of free energies and free enthalpies, corresponding to linear constitutive relations with memory, is presented for isotropic non-magnetic materials. This is a second paper, following recent work on a general tensor theory of isothermal dielectrics and on the form of the minimum free energy. Both papers are based on continuum thermodynamics. For a standard choice of relaxation function, the minimum and maximum free energies are given explicitly, using a method previously developed in a mechanics context. Also, a new family of intermediate free energy functionals is derived for dielectrics. All these are solutions of a constrained optimization problem.

Introduction

A general theory of free energies for dielectric materials under isothermal conditions was given recently [1]. The present work presents more detailed formulae and results for free energies in non-magnetic isotropic materials. We shall derive expressions for the minimum, maximum and other intermediate free energy functionals which also have an extremum property. Two approaches are possible: (1) To present the developments as in mechanics [2], based explicitly on thermodynamics; and (2) To use the method given independently [3-5] for dielectric materials with memory, but with quite different methods, notation and terminology. In this work, as in [1], the fist approach will be adopted but with reference to the connection between the two methods. The intermediate free energies are analogous to quantities known in mechanics [2]. They are new and particularly physically relevant in the context of dielectrics, in that they apply to memory models that are standard for such materials, but not usually applied to viscoelastic behaviour.

Applications of the results of this work, from a physical point of view, include the establishment of bounds on the level of dissipation in the material, using the fact that the total dissipation associated with the minimum(-maximum) free energy is an upper(lower) bound on the actual physical dissipation.

On the matter of notation, vectors and tensors are denoted by lowercase and uppercase boldface characters respectively and scalars by ordinary script. The real line is denoted by $\mathcal{R}$, the non-negative reals by $\mathcal{R}^+$ and the strictly positive reals by $\mathcal{R}^{++}$. Similarly, $\mathcal{R}^-$ is the set of non-positive reals and $\mathcal{R}^{--}$ the strictly negative reals. Complex quantities arise in the frequency domain so we have complex vector spaces for which the dot product involves using the complex conjugate of objects in the dual space. The magnitude squared, denoted by $|.|^2$ refers to the dot product of objects with their complex conjugates.

General Relations

Consider a rigid non-magnetic isotropic dielectric material subject to a varying electric field. Let the body under consideration occupy a volume $\mathcal{B} \subset \mathcal{R}^3$. A typical point in B is x while t is a given time. The electric field on this region is $\mathbf{E}(x,t)$, with electric displacement denoted by $\mathbf{D}(x,t)$. The magnetic field and induction contributions are neglected. The space variables are generally omitted.

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Let $\psi(t)$ be any free energy of the material, for the isothermal case, and $D(t)$ the rate of dissipation. Then the first and second laws of thermodynamics can be written as [1]

$$\dot{\psi} + D = \mathrm{D}.\mathrm{E}, \ D \geq 0. \tag{3.1}$$

Let $\mathrm{E}^t : \mathcal{R}^+ \mapsto \mathcal{V} = \mathcal{R}^3$ be defined by[a]

$$\mathrm{E}^t(s) = \mathrm{E}(t-s), \ s \in \mathcal{R}^+. \tag{3.2}$$

Equation (3.2) gives the history and also the current value $\mathbf{E}(t)$ of the electric field. A given future continuation is denoted by

$$\mathrm{E}^t(s) = \mathrm{E}(t-s), \ s \in \mathcal{R}^{--}. \tag{3.3}$$

Let us define the free enthalpy [1] as

$$\mathcal{F} = \psi - \mathrm{D}.\mathrm{E}. \tag{3.4}$$

In terms of this quantity, (3.1) becomes

$$\dot{\mathcal{F}} + D = -\mathrm{D}.\dot{\mathrm{E}}, \ D \geq 0. \tag{3.5}$$

The relative history E_r^t is defined by

$$\mathrm{E}_r^t(s) = \mathrm{E}^t(s) - \mathrm{E}(t). \tag{3.6}$$

A relative future continuation is also defined by (3.6) for $s \in \mathcal{R}^{--}$.

We define the equilibrium free enthalpy $\mathcal{F}_e(t)$ to be that given for the static history $\mathrm{E}^t(s) = \mathrm{E}(t), \ s \in \mathcal{R}^+$. Therefore,

$$\mathcal{F}_e(t) = \tilde{\mathcal{F}}_e(\mathrm{E}(t)). \tag{3.7}$$

emphasizing that the function $\mathcal{F}_e(t)$ depends only on $\mathbf{E}(t)$.

A. Required properties of a free enthalpy

Let us state the characteristic properties of a free enthalpy, provable within a general framework [1,6-8]:

P1: $\dfrac{\partial \mathcal{F}(t)}{\partial \Lambda(t)} = -\mathrm{D}(t).$ \hfill (3.8)

P2: For any history E_a^t and current value $\mathrm{E}_a(t)$

$$\tilde{\mathcal{F}}(\mathrm{E}_a^t, \mathrm{E}_a(t)) \geq \tilde{\mathcal{F}}_e(\mathrm{E}_a(t)). \tag{3.9}$$

P3: Condition (3.5) holds.

These will be referred to as the Graffi conditions by analogy with those for a free energy in mechanics ([2] for example).

A Linear Memory Model

A special case of the linear model introduced in [1] is described in this section. This is the material consid-

ered in [3-5], namely a passive, homogeneous isotropic non-magnetic dielectric. All kernels are scalar quantities. We have

$$\mathcal{F}(t) = \mathcal{F}_e(t) - \frac{1}{2} \int_0^\infty \int_0^\infty \mathrm{E}_r^t(s).G_{12}(s,u)\mathrm{E}_r^t(u)\,ds\,du \tag{4.1a}$$

$$= \mathcal{F}_e(t) - \frac{1}{2}\int_0^\infty\int_0^\infty \dot{\mathrm{E}}^t(s).\tilde{G}(s,u)\dot{\mathrm{E}}^t(u)\,ds\,du, \tag{4.1b}$$

$$\mathcal{F}_e(t) = -\frac{1}{2}G_\infty \mathrm{E}(t).\mathrm{E}(t), \tag{4.1c}$$

where (4.1b) follows from (4.1a) by partial integrations. Also

$$\dot{\mathrm{E}}^t(u) = \frac{\partial}{\partial t}\mathrm{E}^t(u) = -\frac{\partial}{\partial t}\mathrm{E}^t(u) = -\frac{\partial}{\partial t}\mathrm{E}_r^t(u). \tag{4.2}$$

$\tilde{G}(s,u) = G(s,u) - G_\infty$, and

$$\frac{\partial^2}{\partial s \partial u}G(s,u) \equiv G_{12}(s,u), \tag{4.3a}$$

$$\lim_{s\to\infty} G(s,u) = G_\infty, \ u \in \mathcal{R}^+, \tag{4.3b}$$

$$\lim_{s\to\infty} \frac{\partial}{\partial u}G(s,u) = 0, \ u \in \mathcal{R}^+, \tag{4.3c}$$

$$\lim_{s\to\infty} \frac{\partial}{\partial s}G(s,u) = 0, \ u \in \mathcal{R}^+, \tag{4.3d}$$

$$G(s,u) = G(u,s), \tag{4.3e}$$

with similar limits at large u holding for fixed s. The parameter G_∞ in (4.1a) is defined by (4.3b). Relation (3.8) gives the linear constitutive relation

$$\mathrm{D}(t) = G_\infty \mathrm{E}(t) + \int_0^\infty G'(u)\mathrm{E}_r^t(u)\,du \tag{4.4a}$$

$$= G_0 \mathrm{E}(t) + \int_0^\infty G'(u)\mathrm{E}^t(u)\,du \tag{4.4b}$$

$$= G_\infty \mathrm{E}(t) + \int_0^\infty \tilde{G}(u)\dot{\mathrm{E}}^t(u)\,du \tag{4.4c}$$

$$= \int_0^\infty G(u)\dot{\mathrm{E}}^t(u)\,du, \tag{4.4d}$$

where

$$G(u) = G(0,u), \tag{4.5a}$$

$$G_0 = G(0,0) = G(0), \tag{4.5b}$$

$$\tilde{G}(u) = G(u) - G_\infty, \tag{4.5c}$$

$$G'(u) = \frac{d}{du}G(u). \tag{4.5d}$$

The quantity $G(s)$ is the relaxation function of the material. In writing the final form of (4.4), we are assuming that $\mathrm{E}(-\infty) = \mathrm{E}^t(\infty)$ vanishes; we furthermore assume

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[a]This quantity would be denoted as $\mathrm{E}_-^t(s)$ in [3-5], while the future continuation, defined by (3.3), would be written as $\mathrm{E}_+^t(s)$. The future continuation is referred to in [3] as the recovery field.

that it goes to zero sufficiently strongly so that various integrals, introduced below, exist. The quantity G_∞ is related to the relaxation function through

$$G_\infty = G(s,\infty) = G(0,\infty) = G(\infty). \quad (4.6)$$

We deduce from (3.5), (4.1a) and the time derivative of (4.1b) that

$$D(t) = \frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s).\left[G_1(s,u)+G_2(s,u)\right]\dot{E}^t(u)\,ds\,du \quad (4.7a)$$

$$= -\int_0^\infty\int_0^\infty E_r^t(s).\left[G_{112}(s,u)+G_{212}(s,u)\right]E_r^t(u)\,ds\,du, \quad (4.7b)$$

where subscripts refer to partial differentiation with respect to the first or second argument. Equation (4.7b) follows from (4.7a) by partial integrations, using (4.1a), (4.3), and the fact that $E_r^t(0)$ vanishes. Relation (4.1a), expressed in terms of histories, becomes

$$\mathcal{F}(t) = \frac{1}{2}G_0E(t).E(t) - D(t).E(t) \quad (4.8)$$

$$-\frac{1}{2}\int_0^\infty\int_0^\infty E^t(s).G_{12}(s,u)E^t(u)\,ds\,du.$$

From (3.4), (4.2) and (4.8), we deduce that

$$\psi(t) = \phi_0(t) - \int_0^\infty\int_0^\infty E^t(s).G_{12}(s,u)E^t(u)\,ds\,du \quad (4.9a)$$

$$= U(t) - \frac{1}{2}\int_0^\infty\int_0^\infty E_r^t(s).G_{12}(s,u)E_r^t(u)\,ds\,du, \quad (4.9b)$$

$$= U(t) - \frac{1}{2}\int_0^\infty\int_0^\infty \dot{E}^t(s).\tilde{G}(s,u)\dot{E}^t(u)\,ds\,du, \quad (4.9c)$$

Where

$$\phi_0(t) = \frac{1}{2}G_0E(t).E(t),\ U(t) = D(t).E(t) - \frac{1}{2}G_\infty E(t).E(t) \quad (4.10)$$

The integral terms, with the negative signs included, are non-negative [1]. The total work done by the electric field up to time t is

$$W(t) = \int_{-\infty}^t \dot{D}(u).E(u)\,du \quad (4.11a)$$

$$= D(t).E(t) - \int_{-\infty}^t D(u).\dot{E}(u)\,du. \quad (4.11b)$$

Under the assumption that $\psi(-\infty) = 0$, an integration of (3.1) over $(-\infty,t)$ yields

$$\psi(t) + D(t) = W(t), \quad (4.12)$$

Where

$$D(t) = \int_{-\infty}^t D(u)\,du \geq 0 \quad (4.13)$$

is the total dissipation up to time t. We take G_0 to be equal to the vacuum permittivity ϵ_0 [3-5], giving

$$D(t) = \epsilon_0 E(t) + P(t), \quad (4.14)$$

where, using (4.4b), one sees that the polarization $P(t)$ is given by the causal relationship

$$P(t) = \int_0^\infty G'(u)E^t(u)\,du = \int_{-\infty}^t G'(t-s)E(s)\,ds. \quad (4.15)$$

Then, (4.11a) becomes

$$W(t)\phi_0(t) + W_{int}(t),\ \phi_0(t) = \frac{1}{2}\epsilon_0\left|E(t)\right|^2, \quad (4.16)$$

where $\phi_0(t)$ is the quantity introduced in (4.10) and $W_{int}(t)$ is given by

$$W_{int}(t) = \int_{-\infty}^t \dot{P}(s).E(s)\,ds, \quad (4.17)$$

is the accumulation of energy (density) transferred to the medium at the point under consideration, from the beginning of the pulse-medium interaction until time t. We can write (4.12) as

$$\psi_{int}(t) + D(t) = W_{int}(t), \quad (4.18)$$

where $\psi_{int}(t)$ is given by the integral term in (4.9a).

A. Minimal states

The fundamental definition of the state of a material with memory at time t is the history of the independent field variable and its current value $(E^t, E(t))$. Also, different histories may be members of the same *minimal* state [1]. Two states $\left(E_1^t, E_1(t)\right), \left(E_2^t, E_2(t)\right)$ are equivalent, or in the same minimal state if from a time t onwards, we have

$$D_1(t+s) = D_2(t+s) \text{ if } E_1(t+s) = E_2(t+s), \text{ so } s \geq 0 \quad (4.19)$$

Where D_1, D_2 are defined by (4.4) for these states. Then it follows that

$$\int_0^\infty G'(s+u)\left(E_1^t(u) - E_2^t(u)\right)du = 0,\ s \geq 0 \quad (4.20)$$

A fundamental distinction between materials is that for certain 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 [2,9]. For relaxation functions with only isolated singularities, there is a maximum free energy that is less than the work function $W(t)$ and also a range of related intermediate free energies, which are discussed later. On the other hand, if branch cuts are present, the maximum free energy is $W(t)$.

In this work, we will deal exclusively with the case where the relaxation function has only isolated singularities, so that the minimal states will be non-singleton.

For such materials, the free energy functional is positive semi-definite ([2], page 152).

Note that the statement that $\left(E_1^t, E_1(t)\right)$ and $\left(E_2^t, E_2(t)\right)$ are equivalent is the same as the assertion that $\left(E_d^t, 0\right)$ is

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equivalent to the zero state (0,0), where 0 is the zero in $\mathcal{R}^3$ (and also the zero history), while

$$\mathrm{E}_d^t(s) = \mathrm{E}_1^t(s) - \mathrm{E}_2^t(s). \qquad (4.21)$$

A functional of $(\mathrm{E}^t, \mathrm{E}(t))$ which yields the same value for all members of the same minimal state will be referred to as a functional of the minimal state (abbreviated to FMS) or as a minimal state variable.

Let $\left(\mathrm{E}_1^t, \mathrm{E}_1(t)\right), \left(\mathrm{E}_2^t, \mathrm{E}_2(t)\right)$ be any equivalent states. Then, a free energy is a functional of the minimal state if

$$\psi\left(\mathrm{E}_1^t, \mathrm{E}_1(t)\right) = \psi\left(\mathrm{E}_2^t, \mathrm{E}_2(t)\right).$$

It is not necessary that a free energy have this property, though it holds for the minimum and all related free energies introduced later.

Kernels and Field Variables in the Frequency Domain

For any $f \in L^2(\mathcal{R})$, we denote its Fourier transform $f_F \in L^2(\mathcal{R})$ by[b]

$$f_F(\omega) = \int_{-\infty}^{\infty} f(\xi) e^{-i\omega\xi} d\xi \qquad (5.1a)$$

$$= f_+(\omega) + f_-(\omega), \qquad (5.1b)$$

$$f_+(\omega) = \int_0^{\infty} f(\xi) e^{-i\omega\xi} d\xi, \qquad (5.1c)$$

$$f_-(\omega) = \int_{-\infty}^{\infty} f(\xi) e^{-i\omega\xi} d\xi, \qquad (5.1d)$$

Only real valued functions will be considered so that

$$\overline{f_F}(\omega) = f_F(-\omega), \quad \omega \in \mathcal{R} \qquad (5.2)$$

Where the bar denotes the complex conjugate. For complex values of ω, (5.2) becomes

$$\overline{f_F(\omega)} = f_F(-\overline{\omega}). \qquad (5.3)$$

Functions defined on $\mathcal{R}^+$ are identified with functions on R which vanish identically on $\mathcal{R}^{--}$. For such functions,

$$f_F(\omega) = f_+(\omega) = f_c(\omega) - if_s(\omega), \qquad (5.4)$$

Where $f_c(\omega)$, $f_s(\omega)$ are respectively the Fourier cosine and sine transforms. A property of Fourier transforms which will be used later is

$$f_+(\omega) \xrightarrow[\omega \to \infty]{} \frac{f(0)}{i\omega}, \text{ so that } f_s(\omega) \xrightarrow[\omega \to \infty]{} \frac{f(0)}{\omega} \qquad (5.5)$$

If $(\ )$ is non-zero.

A. The kernel G(u)

We can write the Fourier transforms of $G'(u)$ and $\tilde{G}(u)$ in (4.4) as

$$G_+'(\omega) = G_c'(\omega) - iG_s'(\omega) = \chi_+(\omega) = \chi_c(\omega) - i\chi_s(\omega), \quad (5.6)$$

$$\tilde{G}_+(\omega) = \tilde{G}_c(\omega) - i\tilde{G}_s(\omega).$$

The quantity $\chi_+(\omega)$ is the susceptibility, denoted by $\chi(\omega)$ in [3-5]. By partial integration, one can show that

$$G_+'(\omega) = -(G_0 - G_\infty) + i\omega\tilde{G}_+(\omega), \qquad (5.7)$$

giving, in particular, that

$$\tilde{G}_s(\omega) = \chi_s(\omega) = -\omega\tilde{G}_c(\omega). \qquad (5.8)$$

Observe that

$$G_+'(0) = \int_0^{\infty} G'(s) ds = G_\infty - G_0. \qquad (5.9)$$

Using (5.2), we see that

$$\overline{G_+'}(\omega) = \overline{\chi_+}(\omega) = G_+'(-\omega) = \chi_+(-\omega), \quad (5.10)$$

which will be useful later. By considering periodic behavior in $E^t(s)$, we can show that a consequence of the second law is that ([2], page 140)

$$G_s'(\omega) = \chi_s(\omega) = -\omega\tilde{G}_c(\omega) > 0, \ 0 < \omega < \infty, \quad (5.11)$$

It follows from (5.11) that $G_\infty > G_0$ [1]. We have $G_0 = \in_0 > 0$, so that $G_\infty > 0$.

B. The complex frequency plane and the function H(ω)

We will be considering frequency domain quantities, defined by analytic continuation from integral definitions, as functions on the complex ω plane, denoted by Ω, where

$$\Omega^+ = \left\{\omega \in \Omega \,|\, \mathrm{Im}[\omega] \in \mathcal{R}^+\right\}$$

$$\Omega^{(+)} = \left\{\omega \in \Omega \,|\, Im[\omega] \in \mathcal{R}^{++}\right\}.$$

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

The quantities $f_\pm(\omega)$, defined by (5.1), are analytic in $\Omega^{(\mp)}$ respectively ([2], page 547). Thus, the quantity $G_+'(\omega)$ is analytic on $\Omega^{(-)}$. It will be assumed that $G_+'(\omega)$ is analytic on $\mathcal{R}$ and thus on Ω^-, or more precisely, on an open set containing Ω^-. Also, it will be taken to be analytic at infinity. This function is defined by analytic continuation in regions of Ω^+ where the Fourier integral does not converge. The quantity $G_s'(\omega)$ has singularities in both $\Omega^{(+)}$ and $\Omega^{(-)}$ that are mirror images of each other. It goes to zero at the origin and must also be analytic there. A quantity central to our considerations is defined by

$$H(\omega) = \omega G_s'(\omega) = \omega\chi_s(\omega) = -\omega^2\tilde{G}_c(\omega). \quad (5.13)$$

It is a non-negative, even function of the frequency

and goes to zero quadratically at the origin. The relation (see (5.5))

$$i \lim_{\omega \to \infty} \omega G'_+ (\omega) = \lim_{\omega \to \infty} \omega G'_s (\omega) = G'(0) \quad (5.14)$$

yields

$$G'(0) = H(\infty) = H_\infty . \quad (5.15)$$

For the model considered later, $H(\omega)$ goes to zero at large ω so that $H\infty = 0$. The Fourier transforms of the history and continuation are denoted by $\mathrm{E}^t_+ (\omega)$ and $\mathrm{E}^t_- (\omega)$ respectively[c]. These are particular examples of (5.1c) and (5.1d). The quantity $\mathrm{E}^t_+ (\omega)$ is analytic on $\Omega^{(-)}$ and $\mathrm{E}^t_- (\omega)$ is analytic on $\Omega^{(+)}$. Both are assumed to be analytic on an open set including $\mathcal{R}$. It is further assumed that they are analytic at infinity.

The Fourier transforms of the relative history and continuation, defined by (3.6), have the form

$$\mathrm{E}^t_{r\pm} (\omega) = \mathrm{E}^t_\pm (\omega) \mp \frac{\mathrm{E}(t)}{i\omega^{\mp}}, \quad (5.16)$$

where the notation $\omega^\pm$ is defined as $\omega \pm i\alpha$, $\alpha > 0$. The parameter α is assumed to tend to zero after any integrations have been carried out (see for example [2], page 551). We have

$$\dot{\mathrm{E}}^t_+ (\omega) = \frac{d}{dt} \mathrm{E}^t_+ (\omega) = -i\omega \mathrm{E}^t_+ (\omega) + \mathrm{E}(t) = -i\omega \mathrm{E}^t_{r+} (\omega) \quad (5.17)$$

The second relation follows from (3.2) and an integration by parts in the Fourier integral defining $\mathrm{E}^t_+ (\omega)$. Also, based on arguments from [1] and [2], page 146, for example, we can express the constitutive equation (4.4) in the form

$$\mathrm{D}(t) = G_\infty \mathrm{E}(t) + \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega} \mathrm{E}^t_{r+} (\omega) d\omega$$

$$= G_\infty \mathrm{E}(t) - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega^2} \dot{\mathrm{E}}^t_{r+} (\omega) d\omega \quad (5.18)$$

$$= G_0 \mathrm{E}(t) + \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{H(\omega)}{\omega} \mathrm{E}^t_+ (\omega) d\omega$$

The Work Function

Various forms for the work function, defined by (4.11), are given for the general tensor case in [1]. Those required in this work for scalar kernels are summarized here. The analogous mechanics version of these relations may be found in [2], page 153, for example. It can be shown that

$$W(t) = U(t) - \frac{1}{2} \int_0^\infty \int_0^\infty G_{12} (|u-s|) \mathrm{E}^t_r (u) . \mathrm{E}^t_r (s) \, ds \, du$$

$$= \phi_0 (t) - \frac{1}{2} \int_0^\infty \int_0^\infty G_{12} (|u-s|) \mathrm{E}^t (u) . \mathrm{E}^t (s) \, ds \, du , \quad (6.1)$$

where $U(t)$ and $\phi_0 (t)$ are defined by (4.10). We see from (6.1) that $W(t)$ can be cast in the form (4.9) by putting

$$G_{12} (s,u) = G_{12} (|u-s|) . \quad (6.2)$$

In terms of frequency domain quantities, we find that [1]

$$W(t) = U(t) - \frac{1}{2\pi} \int_{-\infty}^{\infty} \bar{\mathrm{E}}^t_{r+} (\omega) . H(\omega) \mathrm{E}^t_{r+} (\omega) d\omega ,$$

$$= \phi_0 (t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \bar{\mathrm{E}}^t_+ (\omega) . H(\omega) \mathrm{E}^t_+ (\omega) d\omega . \quad (6.3)$$

The quantity $W(t)$-$\mathrm{D}(t) \cdot \mathrm{E}(t)$ can be shown to obey the properties specified in subsection III A of a free enthalpy, with zero dissipation. 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 (4.12). For relaxation functions with only isolated singu-larities, as introduced later, there is a maximum free energy which is a functional of the minimum state and is less that $W(t)$.

Consider the scalar product on the function space of electric fields, defined by [2,5,9-12]

$$\left(\mathrm{E}^t_1 , \mathrm{E}^t_2 \right) = \left(\mathrm{E}^t_{1F} , \mathrm{E}^t_{2F} \right) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{E}^t_1 (s) . G(|s-u|) \mathrm{E}^t_2 (u) \, ds \, du \quad (6.4a)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \bar{\mathrm{E}}^t_{1F} (\omega) . H(\omega) \mathrm{E}^t_{2F} (\omega) d\omega = \left(\mathrm{E}^t_2 , \mathrm{E}^t_1 \right) = \left(\mathrm{E}^t_{2F} , \mathrm{E}^t_{1F} \right) \quad (6.4b)$$

Recalling (5.1), we see that the quantity $\mathrm{E}^t_F (\omega)$ is the Fourier transform of $\mathrm{E}^t (s)$, $s \in \mathcal{R}$ in the time domain. Also, the subscript F in the bracket notation indicates that the frequency domain version is being used. The related norm is

$$\left(\mathrm{E}^t , \mathrm{E}^t \right) = \left\| \mathrm{E}^t \right\|^2 = \left\| \mathrm{E}^t_F \right\|^2 . \quad (6.5)$$

In the notation of (6.5), the work function is given by

$$W(t) = U(t) + \left\| \mathrm{E}^t_r \right\|^2 \quad (6.6a)$$

$$= \phi_0 (t) + \left\| \mathrm{E}^t \right\|^2 , \quad (6.6b)$$

where $\mathrm{E}^t_r (s) = 0$, $s \in \mathcal{R}^{--}$ in (6.6a) and $\mathrm{E}^t (s) = 0$, $s \in \mathcal{R}^{--}$ in (6.6b).

Factorization of $H(\omega)$

We consider materials such that $G'_+ (\omega)$ (or $\tilde{G}_+ (\omega)$) has only a finite number of isolated singularities in $\Omega^{(+)}$. Thus, $H(\omega)$ has only isolated singularities in $\Omega^{(\pm)}$, which are mirror images of each other in the real axis, as ascribed to $G'_s (\omega)$ before (5.13)). This means that it can be put in the form of a ratio of polynomials. We will take the singularities to be a finite number of simple poles. The quantity $H(\omega)$ has a finite number of zeros in $\Omega^\pm (\omega)$, also

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[c]Referring to footnote a, we see that $\mathrm{E}^t_{r\pm} (\omega)$ would be denoted in [3-5] by $\sqrt{2\pi} \hat{\mathrm{E}}^t_{r\mp} (-\omega)$.

mirror images of each other. It is real and non-negative on $\mathcal{R}$, an even function of ω and therefore a function of ω^2, in view of its analyticity about the origin. It vanishes quadratically at the origin. This non-negative quantity can be factorized in general as outlined in [2,13]. Thus, we have that

$$H_+(\omega)H_-(\omega) = H(\omega), \tag{7.1}$$

where

$$H_\pm(\omega) = H_\mp(-\omega) = \overline{H_\mp(\omega)} \tag{7.2a}$$

$$H(\omega) = \left| H_\pm(\omega) \right|^2, \ \omega \in \mathcal{R}. \tag{7.2b}$$

The factorization (7.1) is unique up to multiplication by a phase factor $e^{i\alpha}$, where α is a constant. Relation (7.2a) reduces this arbitrariness to multiplication by a factor ± 1.

The factorization (7.1) is equivalent to a homogeneous Riemann-Hilbert problem on the half-plane [1,3-5].

The quantity $H_+(\omega)$ $(H_-(\omega))$ has all its singularities in $\Omega^{(+)}$ $(\Omega^{(-)})$ and all its zeros in Ω^+ (Ω^-) ([2], page 239). There are many other factorizations, obtained by interchanging some or all of the zeros of $H_+(\omega)$ and $H_-(\omega)$, while retaining the same singularity structure. The different factorizations are labeled by the subscript or superscript f. We have

$$H(\omega) = H_+^f(\omega)H_-^f(\omega), \tag{7.3a}$$

$$H_\pm^f(\omega) = H_\pm^f(-\omega) = \overline{H_\mp^f(\omega)}. \tag{7.3b}$$

Certain types of exchanges must be excluded to ensure that (7.3b) are true [11], ([2], page 338). Each factorization generally yields a different free energy, though there may be exceptions. All these free energies are FMSs [2]. The factorization with no exchange of zeros, which is that given by (7.1), yields the minimum free energy $\psi_m(t)$.

Remark VII.1. 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 quantity ([2], page 363).

Note that the zeros of $H_\pm^f(\omega)$ at the origin play no part in these exchanges.

Remark VII.2. A particularly interesting choice of $\psi_f(t)$, 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 FMSs[d]. It is less than the work function, which is not a FMS for materials with only isolated singularities [2].

If there are N different factorizations of $H(\omega)$, then $f = N$ is chosen to denote the maximum free energy.

Note that there are several (indeed many, for a large number of isolated singularities) different zero exchange pathways leading from the minimum to the maximum free energy.

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

$$\psi(t) = \sum_{f=1}^{N} \lambda_f \psi_f(t), \ D(t) = \sum_{f=1}^{N} \lambda_f D_f(t), \ \sum_{f=1}^{N} \lambda_f = 1, \ \lambda_f \geq 0. \tag{7.4}$$

A particular case of this linear form is the free energy proposed in [11].

Remark VII.3. The set of all free energies at time t associated with a given material is denoted by $\Phi(t)$. The boundary of this set is where one or more of the fundamental properties listed in subsection III A is breaking down; an example, which will arise later, would be where, for a given non-zero history, the rate of dissipation is zero, so that a small shift in its kernel parameters results in it becoming negative.

All the $\psi_f(t)$ emerge from extremum arguments. This is apparent in the case of the minimum free energy for a given state, which is obtained by finding an optimal continuation $E_m^t(s)$, $s \in \mathcal{R}^-$ yielding the maximum recoverable work from this state. Also, the maximum free energy is determined by finding the optimal history $E_M^t(s)$, $s \in \mathcal{R}^+$ which minimizes the work done to achieve the given state. It must be an equivalent state to the given history. In other words, the two histories must be in the same minimal state. The intermediate free energies are also obtained from an extremum principle, but involving an optimization of the history/continuation $E^t(s)$, $s \in \mathcal{R}$, as we shall see in section VIII.

The relevant theoretical developments motivating the results of section VIII are presented in [2], chapter 15 for mechanics; they also apply to dielectrics. We will present an abbreviated version of these arguments, and also demonstrate that the functionals which emerge are in fact free energies, with the required properties. It can be shown that all these quantities, including the intermediate functionals, are on the boundary of $\Phi(t)$ for the material ([2], page 365), which is consistent with the fact that they emerge from an extremum principle. This property is discussed briefly below.

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[d]The minimum and maximum free energies are given also in [5]. The intermediate free energies, introduced in this work, have not been discussed previously in the context of dielectrics, but are analogous to those derived in mechanics in for example [2,10-12].

[e]This behavior, while often used to describe memory behavior of dielectrics, is not usually applied to viscoelastic materials. The singularity structure given by (9.4) corresponds to exponential decay with sinusoidal behavior in the time domain, while viscoelastic materials are generally modeled by simple exponential decay, which in the frequency domain yields simple poles on the positive imaginary axis.

The Free Energy Associated with a Particular Factorization

Let us define the quantities $E_R^t(s)$ and $E_d^t(s)$ by the relation

$$E_R^t(s) = E^t(s) + E_d^t(s), \; s \in \mathcal{R}, \tag{8.1}$$

where $E^t(s)$ is the given history, which is zero for $s \in \mathcal{R}^{--}$. The quantity E_R^t is typically non-zero on $\mathcal{R}$ and E_d^t follows from (8.1). In the frequency domain, the relation becomes

$$E_{RF}^t(\omega) \equiv E_{R+}^t(\omega) + E_{R-}^t(\omega) = E_+^t(\omega) + E_{dF}^t(\omega), \; \omega \in \mathcal{R}, \tag{8.2}$$

where the quantities $E_{R\pm}^t(\omega)$ are particular cases of (5.1c) and (5.1d). Consider the norm $\|E_R\|^2 = \|E_{RF}\|^2$, defined by (6.5). This can be written in a form similar to the quantity $W(\infty)$ in [1], from which the minimum free energy was deduced. We have, from (6.4b) and (6.5), that

$$\|E_{RF}^t\|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\overline{E_+^t(\omega)} + \overline{E_{dF}^t(\omega)} \right] H(\omega) \left[E_+^t(\omega) + E_{dF}^t(\omega) \right] d\omega. \tag{8.3}$$

Let us choose a particular factorization of $H(\omega)$, as given by (7.3). Also, we define [1]

$$H_-^f(\omega) E_+^t(\omega) - q_-^{ft}(\omega) - q_+^{ft}(\omega), \tag{8.4a}$$

$$q_\pm^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_+^t(\omega')}{\omega' - \omega^{\mp}} d\omega'. \tag{8.4b}$$

where the $q_\pm^{ft}(\omega)$ are analytic in $\Omega^{\mp}$, respectively. The singularities of $q_-^{ft}(\omega)$ are the same as those of $H_-^f(\omega)$, as may be perceived by closing the contour in (8.4b) on $\Omega^{(-)}$. Singularities on the real axis are excluded by assumption. Using the factorization in (8.4), we can express $\|E_{RF}\|^2$ in the form

$$\|E_{RF}^t\|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| q_-^{ft}(\omega) - q_+^{ft}(\omega) + H_-^f(\omega) E_{dF}^t(\omega) \right|^2 d\omega. \tag{8.5}$$

Let us further define

$$H_-^f(\omega) E_{dF}^t(\omega) = u_-^{ft}(\omega) - u_+^{ft}(\omega),$$

$$u_\pm^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_{dF}^t(\omega')}{\omega' - \omega^{\mp}} d\omega' \tag{8.6}$$

Note that, by virtue of Cauchy's integral formula,

$$u_-^{ft}(\omega) = q_{d-}^{ft}(\omega) + H_-^f(\omega) E_{d-}^t(\omega) \tag{8.7a}$$

$$= q_{R-}^{ft}(\omega) - q_-^{ft}(\omega) + H_-^f(\omega) E_{d-}^t(\omega), \tag{8.7b}$$

$$u_+^{ft}(\omega) = q_{d+}^{ft}(\omega) = q_{R+}^{ft}(\omega) - q_+^{ft}(\omega), \tag{8.7c}$$

Where $q_{d\pm}^{ft}(\omega)$ are the quantities defined by (8.4b) but with $E_+^t(\omega')$ replaced by

$$E_{d+}^t(\omega') = E_{R+}^t(\omega') - E_+^t(\omega'). \; \text{Also,}$$

$$q_{R\pm}^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_{R+}^t(\omega')}{\omega' - \omega^{\mp}} d\omega'. \tag{8.8}$$

The optimization problem which yields the free energy functional associated with a given factorization of $H(\omega)$ is given as follows ([2], pages 346, 350). We minimize $\|E_{RF}^t\|^2$, subject to the constraint

$$u_-^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_{dF}^t(\omega')}{\omega' - \omega^+} d\omega' = 0. \tag{8.9}$$

The resultant free energy is

$$\psi_f(t) = \phi_0(t) + \|E_f^t\|^2, \tag{8.10}$$

where E_f^t is the history/continuation E_{RF}^t that is the solution of the constrained minimization problem. The formulation of this problem is discussed at length in [2], chapter 15 and earlier papers. In particular, it is shown that each $\psi_f(t)$ has all the required properties of a free energy, which will in any case be shown later for the present context.

Using (8.6), (8.7c) and (8.9) in (8.5) together with proposition 1 of [1], we find that

$$H_-^f(\omega) E_{dF}^t(\omega) = q_+^{ft}(\omega) - q_{R+}^{ft}(\omega), \tag{8.11a}$$

$$\|E_{RF}^t\|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| q_-^{ft}(\omega) - q_{R+}^{ft}(\omega) \right|^2 d\omega \tag{8.11b}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\left| q_-^{ft}(\omega) \right|^2 + \left| q_{R+}^{ft}(\omega) \right|^2 \right] d\omega, \tag{8.11c}$$

where $q_{R+}^{ft}(\omega)$ is given by (8.8). Since $q_{R-}^{ft}(\omega)$ depends only on the given history $E_+^t(\omega)$, the solution to the minimization problem is obtained by choosing $E_{RF}^t(\omega) = E_f^t(\omega)$ to give that

$$q_{R+}^{ft}(\omega) = 0, \tag{8.12}$$

yielding

$$\|E_f^t\|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| q_-^{ft}(\omega) \right|^2 d\omega. \tag{8.13}$$

From (8.11a) and (8.12), we obtain that

$$H_-^f(\omega) E_{dF}^t(\omega) = H_-^f(\omega) E_{RF}^t(\omega) - H_-^f(\omega) E_+^t(\omega) = q_+^{ft}(\omega). \tag{8.14}$$

Then, (8.4a) gives

$$H_-^f(\omega) E_{RF}^t(\omega) = H_-^f(\omega) E_f^t(\omega) = q_-^{ft}(\omega), \tag{8.15}$$

and

$$E_f^t(\omega) = \frac{q_-^{ft}(\omega)}{H_-^f(\omega)} = \frac{1}{2\pi i H_-^f(\omega)} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_+^t(\omega')}{\omega' - \omega^+} d\omega'. \tag{8.16}$$

The observation after (8.4) about the singularities of $q_-^{ft}(\omega)$ and $H_-^f(\omega)$ yield that the singularity structure of $E_f^t(\omega)$ is determined by the zeros of $H_-^f(\omega)$.

Remark VIII.1. *Note that for $f \neq 1$, N, the quantity $H_-^f(\omega)$ has some of its zeros in Ω^- and some in Ω^+. For f = 1, all the zeros of $H_-^f(\omega)$ are in Ω^-, so that $E_f^t(\omega)$ has*

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singularities only in Ω^- and its inverse Fourier transform is thus non-zero only on $\mathcal{R}^-$. This latter quantity is the negative of the optimal continuation, yielding the minimum free energy, which is discussed for the general tensor case in [1]. It can be shown that both the constraint (8.9) and the minimization of $\left\| E_{RF}^t \right\|^2$ result in the same relation, namely (8.16) for $f = 1$.

For $f = N$, all the zeros of $H_-^f(\omega)$ are in Ω^+, which gives that $E_f^t(\omega)$ has singularities only in Ω^+. Therefore, its inverse Fourier transform is non-zero only on $\mathcal{R}^+$ and is the optimal history yielding the maximum free energy. In this case, the quantity $\left\| E_{RF}^t \right\|^2$ to be minimized is the work function and (8.9) is the condition that the optimum history and the given history are in the same minimal state.

For intermediate cases, $E_f^t(\omega)$ is non-zero on $\mathcal{R}$ and minimizes $\left\| E_{RF}^t \right\|^2$, subject to the constraints (8.9), for various factorizations. These constraints are transitional between the two extremes discussed above.

We will see that all of these cases result in free energies that are on the boundary of $\Phi(t)$, defined by remark VII.3. This property is apparent for the minimum and maximum free energies. For these and all intermediate cases, we will see that the corresponding rates of dissipation are positive semi-definite rather than positive definite quadratic forms. They are zero for certain non-zero histories so that small variations in their kernels may lead to negative rates of dissipation, for these histories, in contradiction to the second law, as given by (3.1).

Thus, the fundamental physical content of the constrained optimizations is that they lead to free energies on the boundary of $\Phi(t)$.

The free energy (8.10) has the form

$$\psi_f(t) = \phi_0(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| q_-^{ft}(\omega) \right|^2 d\omega \qquad (8.17a)$$

$$= \phi_0(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \overline{E_f^t}(\omega).H(\omega)E_f^t(\omega)d\omega, \qquad (8.17b)$$

by virtue of (8.13) and (8.15). We have the following relations ([1,10,13,14] for example)

$$\frac{d}{dt}q_+^{ft}(\omega) = -i\omega q_+^{ft}(\omega) - K_f(t), \qquad (8.18a)$$

$$\frac{d}{dt}q_-^{ft}(\omega) = -i\omega q_-^{ft}(\omega) - K_f(t) + H_-^f(\omega)E(t), \qquad (8.18b)$$

$$K_f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} H_-^f(\omega)E_{r+}^t(\omega)d\omega \qquad (8.18c)$$

$$= -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega)}{\omega}\dot{E}_+^t(\omega)d\omega. \qquad (8.18d)$$

and

$$\lim_{|\omega| \to \infty} \omega q_+^{ft}(\omega) = iK_f(t), \qquad (8.19a)$$

$$\lim_{|\omega| \to \infty} \omega q_-^{ft}(\omega) = i\left(K_f(t) - H_{sr}E(t)\right), \qquad (8.19b)$$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} q_+^{ft}(\pm\omega)d\omega = -\frac{1}{2}K_f(t), \qquad (8.19c)$$

$$\frac{1}{2} \int_{-\infty}^{\infty} q^{ft}(\pm\omega)d\omega = -\frac{1}{2}\left(K_f(t) - H_{sr}E(t)\right). \qquad (8.19d)$$

Remark VIII.2. *For the material considered in section IX, the quantity $H(\omega)$ vanishes for large values of ω. Thus, H_{sr} in (8.18) and (8.19) is zero. Also,*

$$\int_{-\infty}^{\infty} \frac{H_-^f(\omega)}{\omega} = 0, \qquad (8.20)$$

as can be seen by closing the contour on $\Omega^{(+)}$, so that, recalling (5.16), it is clear that (8.18c) is replaced by

$$K_f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} H_-^f(\omega)E_+^t(\omega)d\omega. \qquad (8.21)$$

The work function, given by (6.3), takes the form [1]

$$W(t) = \phi_0(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\left| q_-^{ft}(\omega) \right|^2 + \left| q_+^{ft}(\omega) \right|^2\right]d\omega. \qquad (8.22)$$

From (4.12), (8.17) and (8.22), we deduce that the total dissipation corresponding to the minimum free energy is given by

$$D_f(t) = \int_{-\infty}^{t} D_f(u)du = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| q_+^{ft}(\omega) \right|^2 d\omega. \qquad (8.23)$$

Differentiating this relation with respect to t and using (8.18a), (8.19c), gives

$$D_f(t) = \left| K_f(t) \right|^2 \qquad (8.24)$$

Since $K_f(t)$, given by (8.21) can vanish for non-zero histories, $D_f(t)$ is a positive semi-definite rather than a positive definite quadratic form, as noted in remark VIII.1.

We can re-express these results in terms of relative histories [1]. Let us put

$$P^{ft}(\omega) = H_-^f(\omega)E_{r+}^{ft}(\omega) = p_-^{ft}(\omega) - p_+^{ft}(\omega),$$

$$p_\pm^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{P^{ft}(\omega')}{\omega' - \omega^\mp}d\omega' = q_\pm^{ft}(\omega) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{H_-^f(\omega')}{\omega'(\omega' - \omega^\mp)}d\omega'E(t). \qquad (8.25)$$

By closing the contour on Ω^+, it emerges that

$$p_-^{ft}(\omega) = q_-^{ft}(\omega) - \frac{H_-^f(\omega)}{i\omega}E(t), \qquad (8.26a)$$

$$p_+^{ft}(\omega) = q_+^{ft}(\omega). \qquad (8.26b)$$

Also, the work function, given by (8.22), becomes

$$W(t) = U(t) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\left| p_-^{ft}(\omega) \right|^2 + \left| p_+^{ft}(\omega) \right|^2\right]d\omega, \qquad (8.27)$$

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while (8.17b) and (8.23) are given by

$$\psi_f(t) = U(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|\mathrm{p}_-^{ft}(\omega)\right|^2 d\omega, \qquad (8.28a)$$

$$D_f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|\mathrm{p}_+^{ft}(\omega)\right|^2 d\omega. \qquad (8.28b)$$

Equation (8.24) is unchanged.

We now briefly present double integral forms of $\psi_f(t)$, $D_f(t)$ and $D(t)$, which are analogous to (though simpler than) the corresponding formulae in [1] for the minimum free energy in the full tensor case. Using (8.17b) and (8.28a), we can write $\psi_f(t)$ in the forms

$$\psi_f(t) = \phi_0(t) + \frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_+^t(\omega)}.M_f(\omega_1,\omega_2)E_+^t(\omega_2)}{\omega_1^+ - \omega_2^-}d\omega_1 d\omega_2 \quad (8.29a)$$

$$= U(t) + \frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_{r+}^t(\omega_1)}.M_f(\omega_1,\omega_2)E_{r+}^t(\omega_2)}{\omega_1^+ - \omega_2^-}d\omega_1 d\omega_2 \quad (8.29b)$$

$$M_f(\omega_1,\omega_2) = H_+^f(\omega_1)H_-^f(\omega_2), \qquad (8.29c)$$

Also, $D_f(t)$, given by (8.24), can be expressed as

$$D_f(t) = \frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\overline{E_{r+}^t(\omega_1)}.M_f(\omega_1,\omega_2)E_{r+}^t(\omega_2)d\omega_1 d\omega_2 \quad (8.30)$$

From (8.23) and (8.28b), we deduce that

$$D_f(t) = \frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_+^t(\omega_1)}.M_f(\omega_1,\omega_2)E_+^t(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2$$

$$= -\frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_{r+}^t(\omega_1)}.M_f(\omega_1,\omega_2)E_{r+}^t(\omega_2)}{\omega_1^- - \omega_2^+}d\omega_1 d\omega_2. \quad (8.31)$$

One finds that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_+^t(\omega_1)}.M_f(\omega_1,\omega_2)E_+^t(\omega_2)}{\omega_1^+ - \omega_2^-}d\omega_1 d\omega_2 = 0 \quad (8.32)$$

by integrating over ω_2 for example and closing the contour on Ω^-, since $H_+^f(\omega)$ and $E_+^f(\omega)$ have no singularity in the lower half plane. This allows us to write (8.29a) in the explicitly convergent form

$$\psi_f(t) = \phi_0(t) + \frac{i}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\overline{E_+^t(\omega_1)}.\left[M_f(\omega_1,\omega_2) - M_f(\omega_2,\omega_1)\right]E_+^t(\omega_2)}{\omega_1 - \omega_2}d\omega_1 d\omega_2. \quad (8.33)$$

The fact that the integral term is non-negative implies that [1]

$$\triangle^f(\omega) = i\left(\left[H_+^f(\omega)\right]'H_-^f(\omega) - H_+^f(\omega)\left[H_-^f(\omega)\right]'\right) \geq 0,$$

$$\omega \in \mathcal{R}. \qquad (8.34)$$

By invoking (5.17), we see that the quantity $E_{r+}^t(\omega)$ may be replaced by $i\dot{E}_+^t(\omega)/\omega$ in the above double integral expressions.

The free enthalpy $F_f(t)$ corresponding to $\psi_f(t)$ may be deduced from (3.4) to be

$$F_f(t) = \psi_f(t) - D(t).E(t) \qquad (8.35a)$$

$$= -S(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|q_-^{ft}(\omega)\right|^2 d\omega \qquad (8.35b)$$

$$= F_e(t) + \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|P_-^{ft}(\omega)\right|^2 d\omega, \qquad (8.35c)$$

where

$$S(t) = D(t).E(t) - \phi_0(t), \qquad (8.36)$$

and $F_e(t)$ is given by (4.1c). It is easy to show that $F_f(t)$ obeys the Graffi conditions listed in subsection III A. Property P2 is immediately apparent. The relation (4.12) holds by virtue of (8.17), (8.22) and (8.23). The time derivative of (4.12) yields (3.1) with $D_f(t)$ given by (8.24), which is equivalent to P3. Property P1 can be proved with the aid of (8.35b), by showing that

$$\frac{\partial S(t)}{\partial E(t)} = D(t). \qquad (8.37)$$

Remark VIII.3. *It was shown in* [14] *(see also* [2], *page 340) that* $q_-^{ft}(\omega)$, *defined by (8.4), is a function of the minimal state in the sense defined after (4.21). This result transfers to the present context without alteration. From (8.17), we deduce that* $\psi_f(t)$ *is a function of the minimal state as defined by (4.22).*

For the minimum free energy $\psi_m(t)$, we denote $\psi_{int}(t)$, introduced in (4.18), as $\psi_{rec}(t)$, given by

$$\psi_{rec}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|q_-^t(\omega)\right|^2 d\omega, \qquad (8.38)$$

where $q_-^t(\omega)$ is defined by (8.4) for $f = 1$. This is the recoverable energy defined in [3]. The quantity $D_m(t)$, given by (8.23) for $f = 1$, is that referred to as the irrecoverable energy in [3]. Corresponding quantities $\psi_f(t) - \phi_0(t)$ and $D_f(t)$, for each f, may be similarly labeled.

The optimal history/continuation, given by the inverse transform of (8.1), can be shown to have a discontinuity at the origin which is infinite if $H_{sr} = 0$, while at $t = \pm\infty$, it is non-zero ([1,2], page 354).

A Detailed Dielectric Model

We have

$$H(\omega) = \omega\chi_s(\omega) = -\frac{\omega}{2i}\left(\chi_+(\omega) - \overline{\chi_+}(\omega)\right) \geq 0, \ \omega \in \mathcal{R}, \quad (9.1)$$

by virtue of (5.11). As in [3-5], we take the susceptibility to be modeled by a sum of Lorentz oscillators[e]

$$\chi_+(\omega) = \sum_{n=1}^{N}\frac{f_n\omega_{pn}^2}{\omega_n^2 - i\gamma_n\omega - \omega^2}, \qquad (9.2)$$

in terms of the oscillator strength f_n, the plasma frequency ω_{pn}, the resonant frequency ω_n and the damping

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rate γ_n of each oscillator. All of these are positive parameters. It is assumed that

$$\omega_n^2 > \frac{\gamma_n^2}{4}. \tag{9.3}$$

The singularities of $\chi_+(\omega)$ are of course isolated. They are simple poles at

$$\zeta_n = \frac{1}{2}\left[i\gamma_n + \sigma_n\right], \ \zeta_n' = \frac{1}{2}\left[i\gamma_n - \sigma_n\right] = -\overline{\zeta}_n, \tag{9.4}$$

$$\sigma_n = \sqrt{4\omega_n^2 - \gamma_n^2} \ \ n = 1, 2, \ldots, N.$$

Thus, they occur in pairs, equidistant from the positive imaginary axis, as required by (5.3). Separating the poles in (9.2), we can write

$$\chi_+(\omega) = \sum_{n=1}^{N} \frac{f_n \omega_{pn}^2}{\sigma_n} \left\{ \frac{1}{\omega - \zeta_n} - \frac{1}{\omega - \zeta_n'} \right\}. \tag{9.5}$$

In the time domain, this translates into

$$G'(s) = i\sum_{n=1}^{N} \frac{f_n \omega_{pn}^2}{\sigma_n}\left(e^{i\zeta_n s} - e^{i\zeta_n' s}\right), \ s \in \mathcal{R}^+, \tag{9.6}$$

which are decaying exponentials multiplying sine functions [15], so that there will be oscillatory behavior superimposed on the exponential decay. From (9.2) and (9.1), we have

$$H(\omega) = \sum_{n=1}^{N} \frac{f_n \omega_{pn}^2 \gamma_n \omega^2}{\left(\omega_n^2 - \omega^2\right)^2 + \gamma_n^2 \omega^2}, \tag{9.7}$$

which can be written as a ratio of two (factored) polynomials:

$$H(\omega) = H_1 \omega^2 \frac{\prod_{l=1}^{N-1}\left[(\omega - \eta_l)(\omega - \eta_l')(\omega - \overline{\eta}_l)(\omega - \overline{\eta}_l')\right]}{\prod_{l=1}^{N}\left[(\omega - \zeta_l)(\omega - \zeta_l')(\omega - \overline{\zeta}_l)(\omega - \overline{\zeta}_l')\right]} \tag{9.8a}$$

$$H_1 = \sum_{n=1}^{N} f_n \omega_{pn}^2 \gamma_n, \ \omega \in \mathcal{R}, \tag{9.8b}$$

where the denominator of (9.8a) uses the notation of (9.4) while the numerator is factored to yield the zeros of $H(\omega)$; these must occur also in pairs, as in (9.4), so that $\eta_l' = -\overline{\eta}_l$ for each l. We have explicitly included the fact that $H(\omega)$ vanishes quadratically at the origin. Note that the smaller number of zeros reflects the fact that $H(\omega)$ behaves as ω^{-2} for large ω.

The factorization can be carried out by inspection. We obtain

$$H_-(\omega) = h_1 \frac{\prod_{l=1}^{N-1}(\omega - \overline{\eta}_l)(\omega - \overline{\eta}_l')}{\prod_{l=1}^{N}(\omega - \overline{\zeta}_l)(\omega - \overline{\zeta}_l')},$$

$$\overline{\zeta}_l \in \Omega^{(-)}, \ l = 1, 2, \ldots, \ \overline{\eta}_l \in \Omega^{(-)}, l = 1, 2, \ldots N-1. \tag{9.9}$$

$$H_+(\omega) = \overline{H}_-(\omega) = H_-(-\omega),$$

where $h_1^2 = H_1$.

The most general case of a rational function, which is considered in [2,11], can be obtained from (9.8) by allowing singularities to coalesce. As a result of this, some

zeros may also coalesce. Indeed, we cannot exclude the possibility that some of the zeros in (9.8) have a power higher than unity, even if all the singularities are simple poles. For simplicity, it is assumed that this does not happen for our choice of parameters.

Let us define for $l = 1, 2, \ldots, 2N-2$,

$$\alpha_l = \begin{cases} \dfrac{\overline{\zeta_{l+1}}}{2}, & l \text{ odd} \\ \overline{\zeta_{\frac{l}{2}}'}, & l \text{ even} \end{cases}, \ \beta_l = \begin{cases} \dfrac{\overline{\eta_{l+1}}}{2}, & l \text{ odd} \\ \overline{\eta_{\frac{l}{2}}'}, & l \text{ even} \end{cases}, \tag{9.10}$$

and

$$\alpha_{2N-1} = \overline{\zeta_N}, \ \alpha_{2N} = \overline{\zeta_N'}. \tag{9.11}$$

We can write (9.5) as

$$\chi_+(\omega) = \sum_{l=1}^{2N} \frac{g_l}{\omega - \overline{\alpha_l}} = -\sum_{l=1}^{2N} \frac{g_l}{\omega + \alpha_1}, \ \overline{\alpha_l} \in \Omega^{(+)}, \tag{9.12}$$

where (5.10) has been used and

$$g_l = \begin{cases} -\dfrac{f_i \omega_{pi}^2}{\sigma_i}, & i = \dfrac{l+1}{2}, \ l \text{ odd,} \\ \dfrac{f_i \omega_{pi}^2}{\sigma_i}, & i = \dfrac{l}{2}, \ l \text{ even.} \end{cases} \tag{9.13}$$

In this notation, (9.6) becomes

$$G'(s) = i\sum_{l=1}^{2N} g_l e^{i\overline{\alpha}_l s} \tag{9.14}$$

$$= -i\sum_{l=1}^{2N} g_l e^{-i\alpha_l s}. \tag{9.14b}$$

Using (9.14b) in (4.20), we see that two electric field histories are in the same minimal state if and only if

$$E_{1+}^t(\alpha_1) = E_{2+}^t(\alpha_1), \ l = 1, 2, \ldots, 2N. \tag{9.15}$$

Thus, a minimal state is defined by the quantities $(e_1, e_1, \ldots e_{2N})$, where

$$e_l(t) = E_+^t(\alpha_1), \ l = 1, 2, \ldots, 2N. \tag{9.16}$$

Relation (5.3) gives

$$\overline{e_l}(t) = \overline{E_+^t(\alpha_l)} = E_+^t\left(-\overline{\alpha_l}\right), \ l = 1, 2, \ldots, 2N. \tag{9.17}$$

Formula (5.17) for $\omega = \alpha_1$ yields

$$\dot{e}_l(t) = -i\alpha_l e_l(t) + E(t). \tag{9.18}$$

Equation (4.4b) can be written as

$$D(t) = G_0 E(t) - i\sum_{l=1}^{2N} g_i e_i(t) = G_0 E(t) + i\sum_{l=1}^{2N} g_l \overline{e_l}(t), \tag{9.19}$$

with the aid of (9.14), so that

$$\dot{D}(t) = G_0 \dot{E}(t) - i\sum_{l=1}^{2N} g_l \dot{e}_l(t). \tag{9.20}$$

If a free energy or free enthalpy is to depend only on the $e_l(t)$, $l = 1, 2, \ldots, 2N$, then the most general forms of $\tilde{G}(s, u)$ and $G_{12}(s, u)$ in (4.2) and (4.9) are

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$$\tilde{G}(s,u) = -\sum_{i,j=1}^{2N} C_{ij} e^{i\overline{\alpha}_i s - i\alpha_j u}, \tag{9.21}$$

$$G_{12}(s,u) = -\sum_{i,j=1}^{2N} C'_{ij} e^{i\overline{\alpha}_i s - i\alpha_j u}, \quad C'_{ij} = C_{ij} \overline{\alpha}_i \alpha_j, \tag{9.22}$$

where C and C′ are non-negative hermitian matrices. Then, (4.9) gives that

$$\psi(t) = \phi_0(t) + \frac{1}{2}\sum_{i,j=1}^{2N} C'_{ij}\overline{e}_i \cdot e_j$$

$$= U(t) + \frac{1}{2}\sum_{i,j=1}^{2N} C_{ij}\dot{\overline{e}}_i \cdot \dot{e}_j. \tag{9.22}$$

Relation (4.5a) gives

$$\sum_{i=1}^{2N} C_{ij} = -\frac{g_j}{\alpha_j}, \quad j = 1, 2, ..., 2N. \tag{9.23}$$

Taking the complex conjugate of this relation yields

$$\sum_{j=1}^{2N} C_{ij} = -\frac{g_i}{\alpha_i}, \quad i = 1, 2, ..., 2N. \tag{9.24}$$

Equation (3.1) is satisfied if

$$D(t) = \frac{1}{2}\sum_{i,j=1}^{2N} \Gamma_{ij}\dot{\overline{e}}_i \cdot \dot{e}_j, \tag{9.25}$$

$$\Gamma_{ij} = -i(\overline{\alpha}_i - \alpha_j)C_{ij}, \quad i,j = 1, 2, ..., 2N.$$

The matrix with components Γ_{ij} must also be hermitian and non-negative.

Let us now consider the free energies $\psi_f(t)$. We can put (9.9) in the form

$$H_-(\omega) = h_1\omega \frac{\prod_{l=1}^{2N-2}(\omega - \beta_l)}{\prod_{l=1}^{2N}(\omega - \alpha_l)} \tag{9.26a}$$

$$= h_1\omega \sum_{i=1}^{2N} \frac{R_i}{\omega - \alpha_i}, \tag{9.26b}$$

$\alpha_l \in \Omega^{(-)}, l = 1, 2, ..., 2N, \beta_l \in \Omega^{(-)}, l = 1, 2, ..., 2N\text{-}2,$

where

$$R_i = (\omega - \alpha_i)H_-(\omega)|_{\omega = \alpha_i} = h_1\alpha_i \frac{\prod_{l=1}^{2N-2}(\alpha_i - \beta_l)}{\prod_{\substack{l=1 \\ l \neq i}}^{2N}(\alpha_i - \alpha_l)}. \tag{9.27}$$

Also,

$$H_+(\omega) = h_1\omega \frac{\prod_{l=1}^{2N-2}(\omega - \overline{\beta}_l)}{\prod_{l=1}^{2N}(\omega - \overline{\alpha}_l)} \tag{9.28a}$$

$$= -h_1\omega \frac{\prod_{l=1}^{2N-2}(\omega + \gamma_l)}{\prod_{l=1}^{2N}(\omega - \alpha_l)} \tag{9.28b}$$

$$= h_1\omega \sum_{i=1}^{2N} \frac{\overline{R}_i}{\omega - \overline{\alpha}_i} \tag{9.28c}$$

$$= h_1\omega \sum_{i=1}^{2N} \frac{R_i}{\omega + \alpha_i}, \tag{9.28d}$$

where (7.3) has been used. The relationship

$$\sum_{i=1}^{2N} R_i = 0, \tag{9.29}$$

must hold since $H_-(\omega)$ tends to $h_1\omega^{-1}$ at large ω. Therefore, we can also write (9.26b), (9.28c) and (9.28d) as

$$H_-(\omega) = h_1\sum_{i=1}^{2N} \frac{\alpha_i R_i}{\omega - \alpha_i}$$

$$H_+(\omega) = h_1\sum_{i=1}^{2N} \frac{\overline{\alpha}_i \overline{R}_i}{\omega - \overline{\alpha}_i} = h_1\sum_{i=1}^{2N} \frac{\alpha_i R_i}{\omega + \alpha_i} \tag{9.30}$$

We identify also a much larger class of factorizations of $H(\omega)$, determined by interchanging particular β_l in (9.26a) with $\overline{\beta}_l$ in (9.28a). These different factorizations are labeled by the subscript or superscript *f*. Thus,

$$H_-^f(\omega) = h_1\omega \frac{\prod_{l=1}^{2N-2}(\omega - \zeta_l^f)}{\prod_{l=1}^{2N}(\omega - \alpha_l)} \tag{9.31a}$$

$$\sum_1 \overline{\omega \quad \alpha} \tag{9.31b}$$

$$= h_1\sum_{i=1}^{2N} \frac{\alpha_i R_i^f}{\omega - \alpha_i} \tag{9.31c}$$

$\alpha_l \in \Omega^{(-1)}, l = 1, 2, ..., 2N \ \beta_l \in \Omega^{(-1)}, l = 1, 2, ..., 2N\text{-}2,$

$$\zeta_l^f = \lambda_l^f \beta_l + (1 - \lambda_l^f)\overline{\beta}_l, \quad \lambda_l^f = 0 \ or \ 1, \tag{9.31d}$$

$$R_i^f = (\omega - \alpha_i)H_-^f(\omega)|_{\omega = \alpha_i} = h_1\alpha_i \frac{\prod_{l=1}^{2N-2}(\alpha_i - \zeta_l^f)}{\prod_{\substack{l=1 \\ l \neq i}}^{2N}(\alpha_i - \alpha_l)}. \tag{9.31e}$$

Observe that (9.29) also holds for the R^f, a property which has been used in writing (9.31c). There are 2^{2N-2} different factorizations. Referring to the discussion in sections VII and VIII, we note that if all the λ_l^f are equal to one, then $\psi_f(t)$ is the minimum free energy $\psi_m(t)$, while if all are zero, we obtain the maximum free energy $\psi_M(t)$. All other possibilities yield functionals that are intermediate between these two extremes. These observations follow from remark VII.1. Observe that

$$H(\omega) = H_+^f(\omega)H_-^f(\omega) = H_1(\omega)^2 \sum_{i,j=1}^{2N} \frac{\overline{R}_i^f R_j^f}{(\omega - \overline{\alpha}_i)(\omega - \alpha_j)}$$

$$= H_1\omega^2 \sum_{i,j=1}^{2N} \frac{\overline{R}_i^f R_j^f}{\overline{\alpha}_i - \alpha_j}\left\{\frac{1}{(\omega - \overline{\alpha}_i)} - \frac{1}{(\omega - \alpha_j)}\right\}. \tag{9.32}$$

Now, we have the relation

$$\chi_+(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{H(\omega')}{\omega'(\omega' - \omega^-)}d\omega'. \tag{9.33}$$

which follows by applying an integration over $\mathcal{R}$ to

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(9.1) and completing the contour over $\Omega^{(-)}$. The integral over $\chi_+(\omega)$ vanishes. Thus, we have, on integrating over Ω^+,

$$\chi_+(\omega) = \frac{H_1}{\pi} \int_{-\infty}^{\infty} \frac{\omega'}{\omega'-\omega^-} \sum_{i,j=1}^{2N} \frac{\overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} \left\{ \frac{1}{\omega'-\overline{\alpha}_i} - \frac{1}{\omega'-\alpha_j} \right\} d\omega' \quad (9.34a)$$

$$= -2_i H_i \sum_{i,j=1}^{2N} \frac{\overline{\alpha}_i \overline{R_i^f} R_j^f}{(\overline{\alpha}_i - \alpha_j)(\omega - \overline{\alpha}_i)}. \quad (9.34b)$$

The quantity $q_-^{ft}(\omega)$, defined by (8.4), may be evaluated by closing the contour on $\Omega^{(-)}$, giving

$$q_+^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_+^t(\omega')}{\omega'-\omega^+} d\omega' = h_1 \sum_{i=1}^{2N} \frac{\alpha_i R_i^f e_i(\omega)}{\omega - \alpha_i}. \quad (9.35)$$

From (8.4a), we have

$$q_+^{ft}(\omega) = q_-^{ft}(\omega) - H_-^f(\omega) E_+^t(\omega)$$

$$= h_1 \sum_{i=1}^{2N} R_i^f \frac{\left[\alpha_i E_+^t(\alpha_i) - \omega E_+^t(\omega) \right]}{\omega - \alpha_i}, \quad (9.36)$$

which has singularities at those of $E_+^t(\omega)$ in $\Omega^{(+)}$ but none in $\Omega^{(-)}$. These explicit relations allow analytic continuation of $q_\pm^t(\omega)$ to the whole complex plane, excluding singular points. From (8.26a), (9.18), (9.31) and (9.35), we see that the quantity $P_-^{ft}(\omega)$ is given by

$$P_-^{ft}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-^f(\omega') E_{r+}^t(\omega')}{\omega'-\omega^+} d\omega' = i h_1 \sum_{i=1}^{2N} \frac{R_i^f \dot{e}_i(t)}{\omega - \alpha_i}. \quad (9.37)$$

The optimal history/continuation in the frequency domain, which is a special case of (8.16), is given by formulae which are generalizations of those in [2], page 366. We deduce from (8.17b) and (9.35) that

$$\psi_f(t) = \phi_0(t) + i H_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha}_i \alpha_j \overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} \overline{e}_i(t).e_j(t) \quad (9.38a)$$

$$= \phi_0(t) - \frac{1}{2} \int_0^\infty \int_0^\infty E^t(s_1).G_{12}^f(s_1,s_2) E^t(s_2) ds_1 ds_2, \quad (9.38b)$$

Where

$$G_{12}^f(s_1,s_2) = -2i H_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha}_i \alpha_j \overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} e^{i\overline{\alpha}_i s_1 - i\alpha_j s_2}. \quad (9.39)$$

Also, from (8.28a) and (9.37),

$$\psi_f(t) = U(t) + i H_1 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} \overline{e}_i(t).\dot{e}_j(t), \quad (9.40a)$$

$$= U(t) - \frac{1}{2} \int_0^\infty \int_0^\infty \dot{E}^t(s_1).\tilde{G}^f(s_1,s_2) \dot{E}^t(s_2) ds_1 ds_2, \quad (9.40b)$$

Where

$$\tilde{G}^f(s_1,s_2) = -2i H_1 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} e^{i\overline{\alpha}_i s_1 - i\alpha_j s_2}. \quad (9.41)$$

We write (9.38a) and (9.40a) in the form (9.22), giving

$$\psi_f(t) = \phi_0(t) + \frac{1}{2} \sum_{i,j=1}^{2N} C_{fij} \overline{e}_i(t).e_j(t),$$

$$= U(t) + \frac{1}{2} \sum_{i,j=1}^{2N} C_{fij} \overline{e}_i(t).\dot{e}_j(t), \quad C_{fij} = 2i H_1 \frac{\overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j}. \quad (9.42)$$

Comparing (9.34b) with (9.12), we see that

$$g_i = -2i H_1 \sum_{j=1}^{2N} \frac{\overline{\alpha}_i \overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j} = -2i H_1 \sum_{j=1}^{2N} \frac{\alpha_j \overline{R_i^f} R_j^f}{\overline{\alpha}_i - \alpha_j}, \quad (9.43)$$

where (9.29), for the R_i^f, has been used. The relation (4.5a), which yields that $G_2^f(0,s) = G'(s)$, where the latter quantity is given by (9.14), can be confirmed with the aid of (9.41) and (9.43). Relation (9.23), which is equivalent to (4.5a), can be confirmed for C_f.

Recall from (9.16) that the quantities e_1, $i = 1,2,...,2N$ represent a particular minimal state and all the $\psi_f(t)$ are manifestly FMSs.

From (8.18d), (8.21), (9.31b), and (9.31c), we have

$$K_f(t) = -i h_1 \left[\sum_{i=1}^{2N} \alpha_i R_i^f e_i(t) \right] = h_1 \left[\sum_{i=1}^{2N} R_i^f \dot{e}_i(t) \right], \quad (9.44)$$

so that

$$D_f(t) = H_1 \left| \sum_{i=1}^{2N} \alpha_i R_i^f e_i(t) \right|^2 = H_1 \left| \sum_{i=1}^{2N} R_i^f \dot{e}_i(t) \right|^2 \quad (9.45a)$$

$$= H_1 \sum_{i,i=1}^{2N} \overline{R_i^f} \overline{e}_i(t).\dot{e}_j(t) \quad (9.45b)$$

$$= H_1 \sum_{i,i=1}^{2N} \overline{\alpha}_i \alpha_j \overline{R_i^f} R_j^f \overline{e}_i(t).e_j(t). \quad (9.45c)$$

This is in agreement with (9.25). Relations (9.38) and (9.45) can be derived also from (8.29) and (8.30).

Note that $D_f(t)$ vanishes if

$$\sum_{i=1}^{2N} \alpha_i R_i^f e_i(t) = 0. \quad (9.46)$$

Solutions to this equation will exist for non-zero values of $e_i(t)$. Therefore, (9.45b) is a positive semi-definite rather than a positive definite quadratic form, so that the associated matrix will have some zero eigenvalues. If one of these zero eigenvalues were to become slightly negative, then the second law would no longer hold. Thus, the free energy $\psi_f(t)$ is on the boundary of $\Phi(t)$, defined in remark VII.3. This observation is of course a special case of that after (8.24), and relates to remark VIII.1.

A. Sinusoidal histories for non-magnetic materials

Let us consider the formulae (9.44) and (9.38) for histories

$$E^t(s) = A e^{i\omega_0(t-s)} + \overline{A} e^{-i\omega_0(t-s)}, \quad s \in \mathcal{R}^+ \quad (9.47)$$

and

$$E_+^t(\omega) = A \frac{e^{i\omega_0 t}}{i(\omega + \omega_0)} + \overline{A} \frac{e^{-i\omega_0 t}}{i(\omega + \omega_0)}. \quad (9.48)$$

giving that $e_1(t)$, defined by (9.16), has the form

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$$e_l(t) = A\frac{e^{i\omega_0 t}}{i(\omega_0 + \alpha_l)} + \overline{A}\frac{e^{-i\omega_0 t}}{i(\omega_0 + \alpha_l)}. \qquad (9.49)$$

The relation (9.38a) becomes

$$\psi_f(t) = \phi_0(t) + iH_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f} R_j^f}{\overline{\alpha_i} - \alpha_j} \left\{ \begin{array}{c} -\dfrac{A.A}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} e^{2i\omega_0 t} - \dfrac{\overline{A}.\overline{A}}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} e^{-2i\omega_0 t} \\ + \dfrac{A.\overline{A}}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} + \dfrac{\overline{A}.A}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} \end{array} \right\} \qquad (9.50)$$

Also, from (9.44), $K_f(t)$, which determines the rate of dissipation, has the form

$$K_f(t) = -h_1 \sum_{i=1}^{2N} \alpha_i R_i^f \left\{ A\frac{e^{i\omega_0 t}}{(\alpha_i + \omega_0)} + \overline{A}\frac{e^{-i\omega_0 t}}{(\alpha_i - \omega_0)} \right\}. \qquad (9.51)$$

Remark IX.1. *General formulae for the minimum free energy and the associated rate of dissipation were given for sinusoidal histories in [1]. These generalize immediately to apply to $\psi_f(t)$ and $D_f(t)$ by simply replacing $H_\pm(\omega)$ (or the tensor version of these quantities used in [1]) with $H_\pm^f(\omega)$.*

Thus, the formulae for $\psi_f(t)$ and $K_f(t)$ are as follows

$$\psi_f(t) = \phi_0(t) + B_1^f(\omega_0)e^{2i\omega_0 t}A.A + \overline{B_1^f}(\omega_0)e^{-2i\omega_0 t}\overline{A}.\overline{A} + B_2^f(\omega_0)|A|^2,$$

$$B_1^f(\omega_0) = \frac{1}{2}\left\{ X'_+(\omega_0) + \frac{i}{\omega_0}\left[H_-^f(-\omega_0) \right]^2 \right\}, \qquad (9.52)$$

$$B_2^f(\omega_0) = \frac{d}{d\omega_0}\left[\omega_0 X_c(\omega_0) \right] + \Delta^f(\omega_0),$$

$$D_f(t) = |K_f(t)|^2, \quad K_f(t) = H_+^f(\omega_0)Ae^{i\omega_0 t} + H_-^f(\omega_0)\overline{A}e^{-i\omega_0 t}$$

where $\Delta^f(\omega)$ is given by (8.34). It will now be shown that relations (9.50) and (9.51) can also be obtained from these, but after somewhat difficult manipulations. We see from (9.26), (9.28) and remark IX.1 that

$$\left[H_-^f(\omega_0) \right]^2 = H_+^f(\omega_0)H_-^f(\omega_0) = H_1 \omega_0^2 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f}{(\omega_0 - \overline{\alpha_i})(\omega_0 - \alpha_j)}. \qquad (9.53)$$

Referring to (9.34), we have

$$\overline{X}_+(-\omega_0) = X_+(\omega_0) = 2iH_1 \sum_{i,j=1}^{2N} \frac{\alpha_j \overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)(\omega_0 - \alpha_j)}, \qquad (9.54)$$

so that

$$X_+(\omega_0) = -iH_1 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)}\left\{ \frac{\overline{\alpha_i}}{\omega_0 - \overline{\alpha_i}} - \frac{\overline{\alpha_j}}{\omega_0 - \alpha_j} \right\} \qquad (9.55a)$$

$$= -iH_1 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f\left[(\overline{\alpha_i} - \alpha_j)\omega_0 + 2\overline{\alpha_i}\alpha_j \right]}{(\overline{\alpha_i} - \alpha_j)(\omega_0 - \overline{\alpha_i})(\omega_0 + \overline{\alpha_i})}, \qquad (9.55b)$$

We obtain

$$\frac{1}{2}\left[X_+(\omega_0) + \frac{i}{\omega_0}\left[H_-^f(\omega_0) \right]^2 \right] = -iH_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)(\omega_0 - \overline{\alpha_i})(\omega_0 + \alpha_j)}, \qquad (9.56)$$

which agrees with the coefficient of $A.Ae^{2i\omega_0 t}$ in (9.50). From (9.55a), we see that

$$\frac{d}{d\omega_0}\left[\omega_0 X_+(\omega_0) \right] = iH_1 \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)}\left\{ \frac{\overline{\alpha_i}^2}{(\omega_0 - \overline{\alpha_i})^2} + \frac{\alpha_j^2}{(\omega_0 + \alpha_j)^2} \right\} \qquad (9.57)$$

so that

$$\frac{d}{d\omega_0}\left[\omega_0 X_c(\omega_0) \right] = \frac{iH_1}{2} \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)}. \qquad (9.58)$$

$$\left\{ \frac{\overline{\alpha_i}^2}{(\omega_0 - \overline{\alpha_i})^2} + \frac{\alpha_j^2}{(\omega_0 + \alpha_j)^2} + \frac{\overline{\alpha_i}^2}{(\omega_0 + \overline{\alpha_i})^2} + \frac{\alpha_j^2}{(\omega_0 - \alpha_j)^2} \right\}.$$

Also, using (9.30), we see that the quantity $\Delta^f(\omega_0)$, defined by (8.34), is given by

$$\Delta^f(\omega_0) = -iH_1 \sum_{i,j=1}^{2N} \overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f \left\{ \frac{1}{(\omega_0 - \overline{\alpha_i})^2(\omega_0 - \alpha_j)} - \frac{1}{(\omega_0 - \overline{\alpha_i})(\omega_0 - \alpha_j)^2} \right\}$$

$$= -iH_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f}{\overline{\alpha_i} - \alpha_j}\left\{ \frac{1}{\omega_0 - \overline{\alpha_i}}\left(\frac{1}{\omega_0 - \overline{\alpha_i}} - \frac{1}{\omega_0 - \alpha_j} \right) - \frac{1}{(\omega_0 - \alpha_j)}\left(\frac{1}{\omega_0 - \overline{\alpha}} - \frac{1}{\omega_0 - \alpha_j} \right) \right\}. \qquad (9.59)$$

Now, by virtue of (9.29), for the R_i^f, it follows that

$$\sum_{j=1}^{2N} \frac{\alpha_j R_j^f}{\overline{\alpha_i} - \alpha_j} = \sum_{j=1}^{2N} \frac{\overline{\alpha_i} R_j^f}{\overline{\alpha_i} - \alpha_j},$$

$$\sum_{i=1}^{2N} \frac{\overline{\alpha_i} R_i^f}{\overline{\alpha_i} - \alpha_j} = \sum_{j=1}^{2N} \frac{\alpha_j R_j^f}{\overline{\alpha_i} - \alpha_j}. \qquad (9.60)$$

We deduce the relation

$$\Delta^f(\omega_0) = -iH_1\left\{ \sum_{i,j=1}^{2N} \frac{\overline{R_i^f}R_j^f}{\overline{\alpha_i} - \alpha_j}\left[\frac{\overline{\alpha_i}^2}{(\omega_0 - \overline{\alpha_i})^2} + \frac{\alpha_j^2}{(\omega_0 - \alpha_j)^2} \right] - 2\sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f}{(\overline{\alpha_i} - \alpha_j)(\omega_0 - \overline{\alpha_i})(\omega_0 - \alpha_j)} \right\}, \qquad (9.61)$$

Using the symmetry of $\Delta^f(\omega_0)$ with respect to ω_0, we find that

$$\Delta^f(\omega_0) = -\frac{d}{d\omega}\left[\omega_0 X_c(\omega_0) \right]$$

$$+ iH_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f}{\overline{\alpha_i} - \alpha_j}\left\{ \frac{1}{(\omega_0 - \overline{\alpha_i})(\omega_0 - \alpha_j)} + \frac{1}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} \right\}, \qquad (9.62)$$

and therefore

$$B_2^f(\omega_0) = iH_1 \sum_{i,j=1}^{2N} \frac{\overline{\alpha_i}\alpha_j \overline{R_i^f}R_j^f}{\overline{\alpha_i} - \alpha_j}\left\{ \frac{1}{(\omega_0 - \overline{\alpha_i})(\omega_0 - \alpha_j)} + \frac{1}{(\omega_0 + \overline{\alpha_i})(\omega_0 + \alpha_j)} \right\}, \qquad (9.63)$$

which agrees with the constant term (proportional to $|A|^2$) in (9.50).

Summary

The main results are listed below.

1. An isothermal theory of free energies, based on continuum thermodynamics and corresponding to linear constitutive relations with memory, is presented for isotropic non-magnetic materials. For a standard choice of relaxation function, the minimum and maximum free energies are given explicitly.

2. The central new result of this work is the determination of a family of intermediate free energy functionals, for the same relaxation function. These are analogous, though not identical, to those known within a mechanics framework. However, the assumed singularity structure of the frequency domain version of the relaxation function (the susceptibility, for dielectrics) is more relevant,

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in a physical sense, to dielectrics than to mechanics, as discussed in footnote 5, and this singularity structure is the basis of the new results.

3. An important aspect of these developments, from a physical point of view, is that all of these quantities are solutions of a constrained minimization problem, leading to free energy functionals that are on the boundary of the set of all free energies. Going outside of this boundary would yield functionals that do not obey properties imposed by the laws of thermodynamics.

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