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Second Order Approximation For Heat Conduction: Dissipation Principle and Free Energies

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Second-order approximation for heat conduction: dissipation principle and free energies

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In the context of new models of heat conduction, the second-order approximation of Tzou's theory, derived by Quintanilla and Racke, has been studied recently by two of the present authors, where it was proved equivalent to a fading memory material. The importance of determining free energy functionals for such materials, and indeed for any material with memory, is emphasized. Because the kernel does not satisfy certain convexity restrictions that allow us to obtain various traditional free energies for materials with fading memory, it is necessary to restrict the study to the minimum and related free energies, which do not require these restrictions. Thus, the major part of this work is devoted to deriving an explicit expression for the minimum free energy. Simple modifications of this expression also give an intermediate free energy and the maximum free energy for the material. These derivations differ in certain important respects from earlier work on such free energies.

1. Introduction

After Cattaneo's pioneering work [1] on heat conduction with a finite propagation speed, many theories with this property, known also as theories of second sound, have been considered in order to remove the difficulty of infinite propagation speed associated with Fourier's law.

Thus, Tzou, to replace Fourier's law, has suggested in [2] the following constitutive equation for the heat flux vector \mathbf{q} in any point \mathbf{x} of a body $\mathcal{B} \subset \mathcal{R}^3$

$$\mathbf{q}(\mathbf{x}, t + \tau_q) = -k(\mathbf{x})\nabla\theta(\mathbf{x}, t + \tau_\theta), \quad \tau_q > 0, \quad \tau_\theta > 0. \quad (1.1)$$

The scalar function k is positive. In addition, τ_q and τ_θ are delay times related to the heat flux \mathbf{q} and the gradient of temperature $\nabla\theta$, respectively. Obviously, by assuming $\tau_q = 0$ and $\tau_\theta = 0$, Fourier's law follows.

The general form (1.1) cannot be used because, as has been recently observed in [3], it is not in agreement with the second law of thermodynamics. Consequently, several constitutive equations for the heat flux have been obtained by means of Taylor's expansions of (1.1) up to different orders with respect to the parameters τ_q and τ_θ . In this manner, some models have been proposed for which the required compatibility with thermodynamics is satisfied.

It is interesting to observe that the expansion of the left-hand side of (1.1) to first order with respect to the parameter τ_q , while putting $\tau_\theta = 0$ yields Cattaneo's theory [1]

$$\tau_q \dot{\mathbf{q}}(\mathbf{x}, t) + \mathbf{q}(\mathbf{x}, t) = -k(\mathbf{x})\nabla\theta(\mathbf{x}, t). \quad (1.2)$$

If the second-order approximation is considered both for the heat flux and for the temperature gradient, then we obtain the following equation

$$\mathbf{q}(\mathbf{x}, t) + \tau_q \dot{\mathbf{q}}(\mathbf{x}, t) + \frac{\tau_q^2}{2} \ddot{\mathbf{q}}(\mathbf{x}, t) = -k(\mathbf{x}) \left[\nabla\theta(\mathbf{x}, t) + \tau_\theta \nabla\dot{\theta}(\mathbf{x}, t) + \frac{\tau_\theta^2}{2} \nabla\ddot{\theta}(\mathbf{x}, t) \right], \quad (1.3)$$

which was derived in [4,5]. Several authors have considered this equation and studied mathematical problems of existence, uniqueness and stability in relation to it. Some restrictions on the constants τ_q and τ_θ [6,7] have been established by such studies.

In [8], equation (1.3) has been expressed as a fading memory model, so the heat flux depends on the history of the temperature gradient, as for Gurtin & Pipkin's theory [9]. Moreover, a restriction on τ_q and τ_θ given by

$$(2 - \sqrt{3})\tau_\theta < \tau_q < (2 + \sqrt{3})\tau_\theta, \quad (1.4)$$

have been obtained from the requirement of compatibility with thermodynamics.

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. Explicit general formulae for the minimum free energy and associated rate of dissipation were first given in [10]. This was for the scalar viscoelastic case. Generalization to the full tensor case and to other, related, free energies were subsequently given. In addition, the methods developed were adapted to a variety of materials. References to this work and indeed details of these developments may be found in [11].

Free energy functionals are useful in defining the topology of the space of states, when studying stability and related problems for the integrodifferential equations describing the evolution of given materials with memory [12].

Another use for free energies is in modelling dissipation of energy in materials with memory. The minimum and maximum free energies for the material described by (1.3), which are derived in §§4 and 5, provide bounds on energy storage and dissipation in the material under consideration.

Various classical free energies introduced in viscoelasticity and adapted to other materials (see [11,13] and related references), namely those of Dill, Graffi and the new free energy ψ_F , require some restrictions on material properties. These relate to the sign of the kernel and its derivatives, constraints which are satisfied for the Cattaneo–Maxwell material but not for the second-order model of interest here.

The layout of the paper is as follows. In §2, we recall a result obtained in [8], showing the equivalence between the differential equation (1.3) and a constitutive equation with memory. In addition, the second law for closed cycles is stated. In §3, the basic equations required in order to derive the form of the minimum and other related free energies are discussed, whereas in §4,

an explicit expression for the minimum free energy is derived. In §5, it is shown how simple alterations to the resulting formulae yield the maximum free energy and an intermediate free energy. These latter functionals are related to the minimum free energy in the same way as those discussed in [11,14,15], chapters 15 and 16.

2. A fading memory constitutive equation and thermodynamics

We now express (1.3) as a relation between the heat flux and the history of the temperature gradient.

Recall that the Cattaneo–Maxwell equation (1.2) can be written as follow

$$\mathbf{q}(\mathbf{x}, t) = -k(\mathbf{x}) \int_{-\infty}^t \kappa_C(t-s) \nabla \theta(\mathbf{x}, s) ds, \tag{2.1}$$

with kernel

$$\kappa_C(s) = \frac{1}{\tau_q} e^{-(1/\tau_q)s}. \tag{2.2}$$

Recently, in [8], it has been proved that the constitutive relation (1.3) can be rewritten in the form of

$$\begin{aligned} \mathbf{q}(\mathbf{x}, t) &= -\frac{k(\mathbf{x})}{\tau_q^2} \left[\tau_\theta^2 \nabla \theta(t) + 2(\tau_q - \tau_\theta) \int_{-\infty}^t \kappa(t-u) \nabla \theta(\mathbf{x}, u) du \right] \\ &= -\frac{k(\mathbf{x})}{\tau_q^2} \left[\tau_\theta^2 \nabla \theta(t) + 2(\tau_q - \tau_\theta) \int_0^\infty \kappa(s) \nabla \theta^t(\mathbf{x}, s) ds \right], \end{aligned} \tag{2.3}$$

where the kernel κ is given by

$$\kappa(s) = e^{-(1/\tau_q)s} \left[\frac{\tau_\theta}{\tau_q} \cos \frac{s}{\tau_q} + \sin \frac{s}{\tau_q} \right]. \tag{2.4}$$

The quantity $\theta^t(s) = \theta(t-s)$ is the history of the temperature, and the scalar function k is positive.

For the sake of simplicity, we take the kernels to be scalar quantities, though indeed, the results for tensor kernels can also be given, using the methods outlined below.

As noted above, the kernel $\kappa(s)$, given by (2.4), does not in general obey sign restrictions such as $\kappa(s) \geq 0$, $\kappa'(s) \leq 0$, $s \in \mathcal{R}^+$, which are true for (2.2).

The differential problem connected with the constitutive equation (2.3) may be determined from the first law of thermodynamics, given by

$$\rho(\mathbf{x}) \frac{\partial}{\partial t} e(\mathbf{x}, t) = \nabla \cdot \mathbf{q}(\mathbf{x}, t) + \rho(\mathbf{x}) r(\mathbf{x}, t) \tag{2.5}$$

where the functions e , ρ and r denote the internal energy, the mass density and the heat supply, respectively.

The explicit dependence on \mathbf{x} will be mainly omitted henceforth.

For materials with memory such as (2.3), the state $\nabla \theta^t(\cdot)$ is defined by the past history of the temperature gradient. Thus,

$$\nabla \theta^t(s) := \nabla \theta(t-s), \quad s \in [0, \infty), \tag{2.6}$$

whereas a process \mathbf{g}_p of duration $d_p \in \mathcal{R}^+$ is defined by

$$\mathbf{g}_p(t) = \nabla \theta(t), \quad t \in [0, d_p]. \tag{2.7}$$

We denote by Σ the state space and by Π the set of the processes \mathbf{g}_p . The mapping $\hat{\rho} : \Sigma \times \Pi \rightarrow \Sigma$ is the evolution function such that $\sigma^f = \hat{\rho}(\sigma^i, \mathbf{g}_p)$, where σ^i and σ^f are respectively the initial and final states, whereas \mathbf{g}_p is the process connecting these. A closed cycle is defined by the pairs (σ^i, \mathbf{g}_p) such that $\hat{\rho}(\sigma^i, \mathbf{g}_p) = \sigma^i$.

Definition 2.1. A closed cycle is defined by a pair (σ, \mathbf{g}_p) such that $\hat{\rho}(\sigma, \mathbf{g}_p) = \sigma$.

(a) Second law of thermodynamics

On any closed cycle (σ, \mathbf{g}_p) , we have

$$\oint \frac{1}{\theta^2(t)} \mathbf{q}(t) \cdot \mathbf{g}(t) dt \leq 0, \quad (2.8)$$

where the subscript on \mathbf{g}_p has been dropped.

Coleman & Owen in [16] proved a very general result, which in the present context may be stated as follows. If the inequality (2.8) holds for any closed cycle (σ, \mathbf{g}_p) , then there exists a state function $\eta(x, t)$ called entropy such that for any $t \in [0, d_P]$, we have

$$\rho \frac{\partial}{\partial t} \eta(t) \geq \rho \frac{\dot{\epsilon}(t)}{\theta(t)} + \frac{1}{\theta^2(t)} \mathbf{q}(t) \cdot \mathbf{g}(t), \quad \mathbf{g}(t) = \nabla \theta(t). \quad (2.9)$$

In the following, we study the Helmholtz free energy $\psi(t)$ defined by¹

$$\psi(t) = e(t) - \eta(t)\theta(t) \quad (2.10)$$

So, from (2.9) and (2.10), we obtain

$$\theta \rho \frac{\partial}{\partial t} \psi(t) \leq -\rho \eta(t) \frac{\partial}{\partial t} \theta(t) - \frac{1}{\theta(t)} \mathbf{q}(t) \cdot \mathbf{g}(t). \quad (2.11)$$

In the paper, we consider only linear heat conductors. This means that we neglect the space and time dependence of $\theta(\mathbf{x}, t)$ when it is multiplying or dividing other field quantities. It is assumed to be equal to some average temperature, taken to be unity. The space and time dependence of its gradient, $\mathbf{g}(\mathbf{x}, t)$, is however not neglected. We also assume that the mass density ρ is a constant, also taken to be unity. Then, (2.11) becomes

$$\dot{\psi}(t) + \mathbf{q}(t) \cdot \mathbf{g}(t) = -D(t) \leq 0, \quad (2.12)$$

where the dot indicates differentiation with respect to time, or

$$\dot{\psi}(t) + D(t) = -\mathbf{q}(t) \cdot \mathbf{g}(t), \quad D(t) \geq 0. \quad (2.13)$$

The first relation is a form of the first law, given for more general rigid conductors by (2.5) [11, p. 110]. It can be interpreted as follows. The quantity $\dot{\psi}(t)$ is the rate of storage of (thermal) energy, $D(t)$ the rate of energy dissipation, whereas $-\mathbf{q}(t) \cdot \mathbf{g}(t)$ is the total rate of input of energy into the rigid conductor. The inequality imposed on $D(t)$ is in effect the second law.

In this approximation, the inequality (2.8) takes, on any cycle, the new form

$$\oint \mathbf{q}(t) \cdot \mathbf{g}(t) dt \leq 0, \quad (2.14)$$

where equality occurs only for the null cycle. This also follows by integrating (2.13) around any cycle.

Consequently, cycles characterized by histories

$$\mathbf{g} = \mathbf{g}_1 \cos[\omega(t - s)] + \mathbf{g}_2 \sin[\omega(t - s)] \quad (2.15)$$

with $\omega > 0$ and $|\mathbf{g}_1|^2 + |\mathbf{g}_2|^2 > 0$ must satisfy (2.14) as an inequality. When we assume the constitutive equation (2.3) for \mathbf{q} , inequality (2.14) is satisfied if

$$-\frac{k}{\tau_q^2} \frac{\pi}{\omega} (\mathbf{g}_1^2 + \mathbf{g}_2^2) \left[\tau_\theta^2 - \int_0^\infty \kappa(s) \cos(\omega s) ds \right] < 0,$$

therefore

$$\tau_\theta^2 - \int_0^\infty \kappa(s) \cos(\omega s) ds > 0, \quad \omega > 0. \quad (2.16)$$

¹In this framework, because we consider only thermal processes, the Helmholtz and the Gibbs free energies coincide.

Because the half-range cosine Fourier transform of κ is given by

$$\int_0^{\infty} \kappa(s) \cos(\omega s) ds = \kappa_c(\omega) = \frac{2(\tau_q - \tau_\theta)^2 \tau_q^2 \omega^2 + 4(\tau_\theta^2 - \tau_q^2)}{4 + \omega^4 \tau_q^4},$$

the thermodynamic inequality (2.16) is satisfied if and only if the restriction (1.4) holds.

3. Fundamental relations

Let us record, in this section, the basic equations required in order to derive the form of the minimum and other related free energies. We write (2.3) in the form

$$\begin{aligned} \mathbf{q}(t) &= -K_0 \mathbf{g}(t) - \int_{-\infty}^t K'(t-u) \mathbf{g}(u) du \\ &= -K_0 \mathbf{g}(t) - \int_0^{\infty} K'(s) \mathbf{g}^t(s) ds, \end{aligned} \quad (3.1)$$

where

$$K'(s) = k \frac{2(\tau_q - \tau_\theta)}{\tau_q^2} \kappa(s), \quad K(s) = K_0 + \int_0^s K'(u) du \quad \text{and} \quad K_0 = K(0) = k \frac{\tau_\theta^2}{\tau_q^2}, \quad (3.2)$$

where $\kappa(s)$ is given by (2.4). Let us write the kernel $K'(s)$ as follows

$$K'(s) = A e^{\zeta s} + \bar{A} e^{-\bar{\zeta} s}, \quad (3.3)$$

where

$$\zeta = \alpha(1+i), \quad A = k\alpha(1-\rho)(\rho-i), \quad \alpha = \frac{1}{\tau_q}, \quad \rho = \frac{\tau_\theta}{\tau_q} \quad \text{and} \quad K_0 = k\rho^2. \quad (3.4)$$

In the frequency domain, we have

$$K'_+(\omega) = \int_0^{\infty} K'(s) e^{-i\omega s} ds = \frac{iA}{\zeta - \omega} - \frac{i\bar{A}}{\bar{\zeta} + \omega}, \quad (3.5)$$

which indicates a structure of two isolated simple poles placed symmetrically about the upper imaginary axis in the complex plane of frequencies. Unless indicated otherwise, the frequency ω will be assumed to be real.

The theory developed in chapters 15 and 16 of [11] (see also [15]) is a general theory of minimum and related free energies for materials where the memory functions in the frequency domain have arbitrary, within allowed constraints, isolated singularities of any finite order. These developments are presented in notation closely matching viscoelastic materials with linear memory. To facilitate comparison, we express the heat flow theory of interest here in a form similar to such materials. Indeed, this is the motivation for the relations (3.1) above, which indicate a close analogy based on assigning to $-\mathbf{g}^t(\cdot)$ a role corresponding to the strain history.

The form (3.3) is a very special case of the theory considered in [15] and the specified chapters of [11].

There is however a significant difference between the theory for viscoelastic materials and the present case, illustrated in particular by (2.14). The negative of the gradient of temperature is not differentiated with respect to time, as is the case for the strain function in the rate of work done on viscoelastic materials. Therefore, the analogy with viscoelastic materials is not precise and is a source only of general guidance.

In the notation of (3.2), the condition (2.16), imposed by the second law, becomes

$$K_0 + K'_c(\omega) > 0, \quad K'_c(\omega) = \int_0^\infty K'(s) \cos \omega s \, ds. \tag{3.6}$$

In addition, using the discussion after (2.13), together with (3.1)₁, we see that the total thermal work done on the rigid conductor has the form

$$\begin{aligned} - \int_{-\infty}^t \mathbf{q}(u) \cdot \mathbf{g}(u) \, du &= K_0 \int_{-\infty}^t |\mathbf{g}(u)|^2 \, du + \int_{-\infty}^t \int_{-\infty}^u \mathbf{g}(u) \cdot K'(u-s) \mathbf{g}(s) \, ds \, du \\ &= K_0 \int_{-\infty}^t |\mathbf{g}(u)|^2 \, du + \frac{1}{2} \int_{-\infty}^t \int_{-\infty}^t \mathbf{g}(u) \cdot K'(|u-s|) \mathbf{g}(s) \, ds \, du \\ &= K_0 \int_0^\infty |\mathbf{g}^t(u)|^2 \, du + \frac{1}{2} \int_0^\infty \int_0^\infty \mathbf{g}^t(u) \cdot K'(|u-s|) \mathbf{g}^t(s) \, ds \, du \\ &= \frac{K_0}{2\pi} \int_{-\infty}^\infty |\mathbf{g}_+^t(\omega)|^2 \, d\omega + \frac{1}{2\pi} \int_{-\infty}^\infty \bar{\mathbf{g}}_+^t(\omega) \cdot K'_c(\omega) \mathbf{g}_+^t(\omega) \, d\omega \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty \bar{\mathbf{g}}_+^t(\omega) \cdot H(\omega) \mathbf{g}_+^t(\omega) \, d\omega \geq 0, \end{aligned} \tag{3.7}$$

where

$$\left. \begin{aligned} \mathbf{g}_+^t(\omega) &= \int_0^\infty \mathbf{g}^t(u) e^{-i\omega u} \, du, \\ H(\omega) &= K_0 + K'_c(\omega) = K_0 + \frac{1}{2} [K'_+(\omega) + \bar{K}'_+(\omega)] \end{aligned} \right\} \tag{3.8}$$

and

$$|\mathbf{g}(u)|^2 = \mathbf{g}(u) \cdot \mathbf{g}(u).$$

The various forms given in (3.7) follow by virtue of a standard development as outlined in for example section 6.5 of [11]. Note that the quantity $H(\omega)$ is non-negative by virtue of (3.6)₁, which is an expression of the second law. It can therefore be concluded that

$$- \int_{-\infty}^t \mathbf{q}(u) \cdot \mathbf{g}(u) \, du \geq 0. \tag{3.9}$$

We can write (3.1)₁ in the frequency domain as

$$\begin{aligned} \mathbf{q}(t) &= -K_0 \mathbf{g}(t) - \frac{1}{2\pi} \int_{-\infty}^\infty \bar{K}'_+(\omega) \mathbf{g}_+^t(\omega) \, d\omega \\ &= -\frac{K_0}{\pi} \int_{-\infty}^\infty \mathbf{g}_+^t(\omega) \, d\omega - \frac{1}{2\pi} \int_{-\infty}^\infty \bar{K}'_+(\omega) \mathbf{g}_+^t(\omega) \, d\omega. \end{aligned} \tag{3.10}$$

Observe that the first term on the right of (3.10)₂ has a factor of 2 over what one might expect. This term emerges from the time domain version by integrating over the lower frequency complex plane in a contour yielding zero, noting however that the infinite part of the contour makes a non-zero contribution, which can be evaluated using

$$\mathbf{g}_+^t(\omega) \sim \frac{\mathbf{g}(t)}{i\omega}, \tag{3.11}$$

at large ω . This contribution must be subtracted from the contour integral and the result shown in (3.10)₂ emerges. Using a manipulation discussed in [11, p. 146], and earlier references therein, we can replace (3.10)₂ by

$$\begin{aligned} \mathbf{q}(t) &= -\frac{K_0}{\pi} \int_{-\infty}^\infty \mathbf{g}_+^t(\omega) \, d\omega - \frac{1}{2\pi} \int_{-\infty}^\infty [\bar{K}'_+(\omega) + K'_+(\omega)] \mathbf{g}_+^t(\omega) \, d\omega \\ &= -\frac{1}{\pi} \int_{-\infty}^\infty H(\omega) \mathbf{g}_+^t(\omega) \, d\omega. \end{aligned} \tag{3.12}$$

On substituting (3.3) into (3.1)₁, we obtain

$$\mathbf{q}(t) = -K_0 \mathbf{g}(t) - A \mathbf{g}_+^t(-\zeta) - \bar{A} \mathbf{g}_+^t(\bar{\zeta}). \tag{3.13}$$

319 Observe that $\mathbf{g}_+^t(\bar{\zeta}) = \overline{\mathbf{g}_+^t(-\zeta)}$. The relation

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$$\frac{d}{dt} \mathbf{g}_+^t(-\zeta) = \mathbf{g}(t) + i\zeta \mathbf{g}_+^t(-\zeta). \tag{3.14}$$

322 will be used later.

323 The property that the histories $\mathbf{g}_1^t(s)$ and $\mathbf{g}_2^t(s)$ are in the same minimal state has the standard
324 form which follows from (3.1)₁, namely

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$$\mathbf{g}_1(t) = \mathbf{g}_2(t), \quad \int_0^\infty K'(s+u) \mathbf{g}_1^t(u) du = \int_0^\infty K'(s+u) \mathbf{g}_2^t(u) du, \quad s \geq 0. \tag{3.15}$$

327 It can be shown that the second relation is equivalent to the requirements [11, p. 359]

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$$\mathbf{g}_{1+}^t(-\zeta) = \mathbf{g}_{2+}^t(-\zeta), \quad \mathbf{g}_{1+}^t(\bar{\zeta}) = \mathbf{g}_{2+}^t(\bar{\zeta}), \tag{3.16}$$

330 so that an equivalence class of histories is characterized by the triplet $V = (\mathbf{g}_+^t(-\zeta), \mathbf{g}_+^t(\bar{\zeta}), \mathbf{g}(t))$.
331 A functional of a minimal state containing $\mathbf{g}^t(s)$ must have the property that its dependence on
332 $\mathbf{g}^t(s)$ is expressible as a dependence only on V . This is, in particular, true of the minimum free
333 energy discussed below.

334 We can show that

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336
$$\left. \begin{aligned} H(\omega) &= \frac{N(\omega)}{D(\omega)}, \\ N(\omega) &= a\omega^4 + b\omega^2 + c, \quad a = K_0, \quad b = i(\bar{A}\bar{\zeta} - A\zeta) - K_0(\zeta^2 + \bar{\zeta}^2), \\ c &= [K_0|\zeta|^2 - i(\bar{A}\zeta - A\bar{\zeta})]|\zeta|^2 \\ D(\omega) &= (\zeta - \omega)(\zeta + \omega)(\bar{\zeta} - \omega)(\bar{\zeta} + \omega) \\ &= (\zeta^2 - \omega^2)(\bar{\zeta}^2 - \omega^2) = |\zeta - \omega|^2 |\zeta + \omega|^2 \geq 0. \end{aligned} \right\} \tag{3.17}$$

337 and
338 The polynomial $N(\omega)$ is clearly real for real ω . It must also be non-negative, which is the constraint
339 imposed by the second law, as discussed in the context of (3.6) and (3.7). Note that it is positive
340 for large values of ω . To ensure non-negativity for all real ω , the form of $N(\omega)$ given by (3.17)₂,
341 expressed as a function of ω^2 , cannot have real roots. These roots are given by

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$$\eta^2 = \frac{1}{2a} [-b \pm \sqrt{b^2 - 4ac}], \tag{3.18}$$

344 so that we must have

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$$b^2 - 4ac \leq 0. \tag{3.19}$$

347 For ζ and A given by (3.4), we obtain

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$$a = k\rho^2 > 0, \quad b = -2k\alpha^2(\rho - 1)^2 < 0 \quad \text{and} \quad c = 4\alpha^4 k > 0 \tag{3.20}$$

350 and

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352
$$\begin{aligned} b^2 - 4ac &= 4k^2\alpha^4[(\rho - 1)^4 - 4\rho^2] \\ &= 4k^2\alpha^4(\rho^2 + 1)(\rho - 2 + \sqrt{3})(\rho - 2 - \sqrt{3}) \leq 0. \end{aligned} \tag{3.21}$$

353 This inequality yields

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$$2 - \sqrt{3} < \rho < 2 + \sqrt{3}, \tag{3.22}$$

356 which is (1.4), as expected.

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We can write $N(\omega)$ in a form similar to $D(\omega)$

$$N(\omega) = K_0(\eta - \omega)(\eta + \omega)(\bar{\eta} - \omega)(\bar{\eta} + \omega) = K_0(\eta^2 - \omega^2)(\bar{\eta}^2 - \omega^2) = K_0|\eta - \omega|^2|\eta + \omega|^2 \geq 0. \tag{3.23}$$

The quantity $-b/(2a)$ is always positive for values specified by (3.20). The roots given by (3.18) are therefore in the first and fourth quadrant of the complex plane. These have the form

$$\left. \begin{aligned} \eta^2 = x + iy, \quad x = \frac{\alpha^2}{\rho^2}(\rho - 1)^2 \\ y = \frac{\alpha^2}{\rho^2}\sqrt{\rho^2 + 1}\sqrt{4\rho - \rho^2 - 1}. \end{aligned} \right\} \tag{3.24}$$

It follows that

$$x^2 + y^2 = 4\frac{\alpha^4}{\rho^2}. \tag{3.25}$$

If $\eta = u + iv$, then

$$\left. \begin{aligned} u^2 = \frac{1}{2}(\sqrt{x^2 + y^2} + x) = \frac{1}{2}\frac{\alpha^2}{\rho^2}(\rho^2 + 1) \\ v^2 = \frac{1}{2}(\sqrt{x^2 + y^2} - x) = \frac{1}{2}\frac{\alpha^2}{\rho^2}(4\rho - \rho^2 - 1). \end{aligned} \right\} \tag{3.26}$$

We choose $u > 0, v > 0$, so that η is in the first quadrant and

$$u = \frac{1}{\sqrt{2}}\frac{\alpha}{\rho}\sqrt{\rho^2 + 1}, \quad v = \frac{1}{\sqrt{2}}\frac{\alpha}{\rho}\sqrt{4\rho - \rho^2 - 1}. \tag{3.27}$$

The thermodynamic constraint expressed by the inequality in (3.21) can be written in the form

$$4\rho - \rho^2 - 1 \geq 0, \tag{3.28}$$

which will be useful later in various contexts.

The quantity $H(\omega)$ can be factorized as follows:

$$\left. \begin{aligned} H(\omega) &= H_+(\omega)H_-(\omega), \\ H_+(\omega) &= \sqrt{K_0}\frac{(\omega - \eta)(\omega + \bar{\eta})}{(\omega - \zeta)(\omega + \bar{\zeta})} \\ H_-(\omega) &= \sqrt{K_0}\frac{(\omega + \eta)(\omega - \bar{\eta})}{(\omega + \zeta)(\omega - \bar{\zeta})} = \bar{H}_+(\omega), \end{aligned} \right\} \tag{3.29}$$

where the singularities and zeros of $H_+(\omega)$ are in the upper half of the complex plane, whereas $H_-(\omega) = \bar{H}_+(\omega)$ has all singularities and zeros in the lower half.

We note in passing that the number of non-trivial zeros of $H(\omega)$ in the present case is twice that in the corresponding viscoelastic problem [11,14,15]. This is related to the fact that $H(0)$ is not zero.

4. The minimum free energy

We now use the results of §3 to derive an explicit expression for the minimum free energy.

With the aid of the Plemelj formulae [11,17], we can show that the thermal work given by the negative of (3.7) can be expressed in the form (see for example [10] and [11], page 243)

$$\left. \begin{aligned} - \int_{-\infty}^t \mathbf{q}(u) \cdot \mathbf{g}(u) \, du &= \frac{1}{2\pi} \int_{-\infty}^{\infty} [|\mathbf{p}_+^t(\omega)|^2 + |\mathbf{p}_-^t(\omega)|^2] \, d\omega, \\ \mathbf{p}_{\pm}^t(\omega) &= -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_-(\omega_1) \mathbf{g}_{\pm}^t(\omega_1)}{\omega_1 - \omega^{\mp}} \, d\omega_1 \\ \text{and} \quad |\mathbf{p}_{\pm}^t(\omega)|^2 &= \bar{\mathbf{p}}_{\pm}^t(\omega) \cdot \mathbf{p}_{\pm}^t(\omega), \end{aligned} \right\} \quad (4.1)$$

where the notation ω^{\pm} is introduced in [10] and widely used in subsequent work.

It is convenient to use histories of the temperature gradient in the present work, rather than relative histories [10,11,15]. In particular, histories are used in the definition of $\mathbf{p}_{\pm}^t(\omega)$, so that these quantities are most closely related to those in [10]². We note however that the quantities $\mathbf{p}_{\pm}^t(\omega)$ used here differ somewhat from those in [10] because of the fact that $H(0)$ is not zero in the present model.

Using arguments presented in various papers, notably [10,14] and chapter 10 of [11], we can deduce that the minimum free energy is given by

$$\psi_m(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} |\mathbf{p}_-^t(\omega)|^2 \, d\omega \geq 0. \quad (4.2)$$

Expression (4.2), relating to a given state of the material at time t , arises, for this and all other cases considered, from the very general requirement that it is equal to the maximum recoverable work from that state, a requirement which emerges from the axiomatic formulation of the thermodynamics of materials with memory ([11,16], ch. 4).

The time derivative of relation (4.1)₁ is in fact the energy balance equation or first law of thermodynamics, given by (2.13), in the context of the minimum free energy. We can write it as

$$\left. \begin{aligned} \dot{\psi}_m(t) + D_m(t) &= -\mathbf{q}(t) \cdot \mathbf{p}(t) \\ \text{and} \quad D_m(t) &= \frac{d}{dt} \frac{1}{2\pi} \int_{-\infty}^{\infty} |\mathbf{p}_+^t(\omega)|^2 \, d\omega \geq 0. \end{aligned} \right\} \quad (4.3)$$

By following steps closely related to those in [10], we can show that the rate of dissipation associated with the minimum free energy is

$$\left. \begin{aligned} D_m(t) &= |\mathbf{J}(t)|^2 \\ \text{and} \quad \mathbf{J}(t) &= -\frac{1}{2\pi} \int_{-\infty}^{\infty} H_-(\omega) \mathbf{g}_+^t(\omega) \, d\omega - \frac{1}{2} \sqrt{K_0} \mathbf{g}(t) \\ &= -\frac{1}{2\pi} \int_{-\infty}^{\infty} H_-(\omega) \left[\mathbf{g}_+^t(\omega) - \frac{\mathbf{g}(t)}{i\omega} \right] \, d\omega - H_-(0) \mathbf{g}(t). \end{aligned} \right\} \quad (4.4)$$

The term with $H_-(0)$ is not present in the developments of [10]. The non-negativity of $D_m(t)$, which is clear from (4.4), is an expression of the second law.

We can write $H_{\pm}(\omega)$, given by (3.29) in the form

$$\left. \begin{aligned} H_+(\omega) &= \sqrt{K_0} \left[1 - \frac{M}{\omega - \zeta} + \frac{\bar{M}}{\omega + \bar{\zeta}} \right], \\ H_-(\omega) &= \sqrt{K_0} \left[1 + \frac{M}{\omega + \zeta} - \frac{\bar{M}}{\omega - \bar{\zeta}} \right] \\ \text{and} \quad M &= \frac{(\eta - \zeta)(\bar{\eta} + \bar{\zeta})}{(\zeta + \bar{\zeta})}. \end{aligned} \right\} \quad (4.5)$$

²Note that the quantities $\mathbf{p}_{\pm}^t(\omega)$ here are designated as $\mathbf{q}_{\pm}^t(\omega)$ in [10]. We avoid this notation because of possible confusion with the heat flow $\mathbf{q}(t)$.

One can show that

$$M = \frac{1}{2\alpha} [|\eta|^2 + \zeta(\eta - \bar{\eta}) - \zeta^2] = \frac{\alpha}{\rho} [1 - e + i(e - \rho)] \quad (4.6)$$

$$\text{and } e = \sqrt{2\rho - \frac{\rho^2 + 1}{2}}.$$

Closing the contour of (3.12)₂ on $\Omega^{(-)}$, and using (4.5), we obtain

$$\mathbf{q}(t) = -K_0 \mathbf{g}(t) + 2iK_0 \left[1 + \frac{M}{2\zeta} - \frac{\bar{M}}{\zeta - \bar{\zeta}} \right] M \mathbf{g}_+^t(-\zeta) - 2iK_0 \left[1 - \frac{M}{\bar{\zeta} - \zeta} + \frac{\bar{M}}{2\bar{\zeta}} \right] \bar{M} \mathbf{g}_+^t(\bar{\zeta}). \quad (4.7)$$

Comparing with (3.13), it will be observed that

$$A = -2iK_0 \left[M + \frac{M^2}{2\zeta} - \frac{|M|^2}{\zeta - \bar{\zeta}} \right], \quad (4.8)$$

where A is defined in (3.4). This relation can be confirmed with the help of (4.6).

We deduce from (4.1)₂ and (4.5) that

$$\mathbf{p}_-^t(\omega) = -\sqrt{K_0} \left[M \frac{\mathbf{g}_+^t(-\zeta)}{\omega + \zeta} + \bar{M} \frac{\mathbf{g}_+^t(\bar{\zeta})}{\omega - \bar{\zeta}} \right], \quad (4.9)$$

by closing the contour on $\Omega^{(-)}$. Let us define

$$\left. \begin{aligned} \mathbf{g}_+^t(-\zeta) &= \mathbf{g}_r^t(\alpha) + i\mathbf{g}_i^t(\alpha), \\ \mathbf{g}_r^t(\alpha) &= \int_0^\infty \mathbf{g}^t(s) e^{-\alpha s} \cos(\alpha s) ds \\ \mathbf{g}_i^t(\alpha) &= \int_0^\infty \mathbf{g}^t(s) e^{-\alpha s} \sin(\alpha s) ds, \end{aligned} \right\} \quad (4.10)$$

with the aid of (3.1)₁

Using (4.2) and (4.9), the minimum free energy can be written in the form

$$\psi_m(t) = iK_0 \left\{ \frac{[|M|^2 |\mathbf{g}_+^t(-\zeta)|]^2}{i\alpha} - \frac{[M \mathbf{g}_+^t(-\zeta)]^2}{2\zeta} + \frac{[\bar{M} \mathbf{g}_+^t(\bar{\zeta})]^2}{2\bar{\zeta}} \right\}, \quad (4.11)$$

where

$$[M \mathbf{g}_+^t(-\zeta)]^2 = M^2 \mathbf{g}_+^t(-\zeta) \cdot \mathbf{g}_+^t(-\zeta), \quad (4.12)$$

and similarly for the complex conjugate term and others introduced below. Let us define

$$M = \frac{\alpha}{\rho} (\lambda + i\mu), \quad \lambda = 1 - e \quad \text{and} \quad \mu = e - \rho. \quad (4.13)$$

Then, $\psi_m(t)$ can be expressed as

$$\left. \begin{aligned} \psi_m(t) &= \frac{1}{2} \int_0^\infty \int_0^\infty \mathbf{g}^t(s) \cdot G(s, s') \mathbf{g}^t(s') ds ds' \\ \text{and } G(s, s') &= 2K_0 Re \left\{ e^{i(\zeta s - \bar{\zeta} s')} \frac{|M|^2}{\alpha} - i e^{i\zeta(s+s')} \frac{M^2}{\zeta} \right\} \\ &= 2K_0 e^{-\alpha(s+s')} \frac{\alpha}{\rho^2} \left\{ (\lambda^2 + \mu^2) \cos \alpha(s - s') \right. \\ &\quad \left. - \frac{1}{2} (\lambda^2 - \mu^2 - 2\lambda\mu) \cos \alpha(s + s') \right. \\ &\quad \left. + \frac{1}{2} (\lambda^2 - \mu^2 + 2\lambda\mu) \sin \alpha(s + s') \right\} \\ &= 2K_0 e^{-\alpha(s+s')} \frac{\alpha}{\rho^2} \{ 2[2\rho - e(1 + \rho)] \cos \alpha(s - s') \\ &\quad - [3\rho - \rho^2 - 2e] \cos \alpha(s + s') \\ &\quad + [1 + 2e\rho - 3\rho] \sin \alpha(s + s') \}, \end{aligned} \right\} \quad (4.14)$$

in terms of the quantities α , ρ and K_0 defined in (3.4) and e which is introduced in (4.6). Either by expanding the trigonometrical functions in (4.14) or by using (4.10) in (4.11), we can also express the minimum free energy as the quadratic form

$$\left. \begin{aligned} \psi_m(t) &= \frac{K_0 \alpha}{\rho^2} h^\top \mathbf{A} h, \quad h = (\mathbf{g}_r^t(\alpha), \mathbf{g}_i^t(\alpha)) \\ \text{and } \mathbf{A} &= \frac{1}{2} \begin{pmatrix} \lambda^2 + 3\mu^2 + 2\lambda\mu & \lambda^2 - \mu^2 + 2\lambda\mu \\ \lambda^2 - \mu^2 + 2\lambda\mu & 3\lambda^2 + \mu^2 - 2\lambda\mu \end{pmatrix} \geq 0. \end{aligned} \right\} \quad (4.15)$$

The non-negativity property of the matrix \mathbf{A} can be shown for general values of λ and μ . In the present context,

$$\mathbf{A} = \begin{pmatrix} \rho(1 + \rho - 2e) & 1 - 3\rho + 2e\rho \\ 1 - 3\rho + 2e\rho & 7\rho - \rho^2 - 4e - 2e\rho \end{pmatrix}. \quad (4.16)$$

The rate of dissipation associated with $\psi_m(t)$ is given by (4.4) which, in the light of (4.5), becomes

$$\begin{aligned} D_m(t) &= K_0 [\mathbf{g}(t) + iM\mathbf{g}_+^t(-\zeta) - i\bar{M}\mathbf{g}_+^t(\bar{\zeta})]^2 \\ &= K_0 \left\{ \mathbf{g}^2(t) - 2iM\mathbf{g}_+^t(-\zeta) \cdot \mathbf{g}(t) + 2i\bar{M}\mathbf{g}_+^t(\bar{\zeta}) \cdot \mathbf{g}(t) \right. \\ &\quad \left. + 2|M|^2 |\mathbf{g}_+^t(-\zeta)|^2 - [M\mathbf{g}_+^t(-\zeta)]^2 - [\bar{M}\mathbf{g}_+^t(\bar{\zeta})]^2 \right\}. \end{aligned} \quad (4.17)$$

It is of interest to confirm that (4.3)₁ holds for the above formulae. Using (3.14) and (4.7), we see that

$$\begin{aligned} \dot{\psi}_m(t) &= iK_0 \left\{ \frac{|M|^2}{i\alpha} [\mathbf{g}_+^t(\bar{\zeta}) + \mathbf{g}_+^t(-\zeta)] - \frac{M^2 \mathbf{g}_+^t(-\zeta)}{\zeta} + \frac{\bar{M}^2 \mathbf{g}_+^t(\bar{\zeta})}{\bar{\zeta}} \right\} \cdot \mathbf{g}(t) \\ &\quad - K_0 \left\{ 2|M|^2 |\mathbf{g}_+^t(-\zeta)|^2 - [M\mathbf{g}_+^t(-\zeta)]^2 - [\bar{M}\mathbf{g}_+^t(\bar{\zeta})]^2 \right\} \\ &= -\mathbf{q}(t) \cdot \mathbf{g}(t) - D_m(t). \end{aligned} \quad (4.18)$$

We observe that this relation is satisfied in a somewhat different way from that for viscoelastic problems and indeed for thermal memory problems without the Fourier term. For these other materials, the quantity $\dot{\psi}_m(t)$ generates the rate of dissipation $D_m(t)$ and the rate of work. In the present case, $\dot{\psi}_m(t)$ generates those parts of the rate of dissipation and rate of work $-\mathbf{q}(t) \cdot \mathbf{g}(t)$ which are quadratic in M and \bar{M} , whereas the terms in the rate of dissipation which are linear in M , \bar{M} or independent of these quantities provide the remainder of the rate of work.

In relation to this difference, consider the quantity $G(s, s')$ in (4.14). The quantity $G(s, 0) = G(0, s)$ in viscoelasticity is the relaxation function of the material. In the present case, using (4.7) and (4.14)₂, we see that

$$\mathbf{q}(t) = -K_0 \mathbf{g}(t) - \int_0^\infty G(0, s) \mathbf{g}^t(s) ds + 2iK_0 M \int_0^\infty e^{i\zeta s} \mathbf{g}^t(s) ds - 2iK_0 \bar{M} \int_0^\infty e^{-i\bar{\zeta} s} \mathbf{g}^t(s) ds, \tag{4.19}$$

so that $G(0, s)$ is that part of the relaxation function that is quadratic in M and \bar{M} .

The quantity $D_m(t)$ can be expressed as

$$\left. \begin{aligned} D_m(t) &= K_0 \mathbf{g}^2(t) + 4K_0 \frac{\alpha}{\rho} \mathbf{g}(t) \cdot [\mu \mathbf{g}_r^t(\alpha) + \lambda \mathbf{g}_i^t(\alpha)] \\ &\quad + \frac{1}{2} \int_0^\infty \int_0^\infty \mathbf{g}^t(s) \cdot L(s, s') \mathbf{g}^t(s') ds ds' \\ \text{and} \quad L(s, s') &= 4K_0 \operatorname{Re} \left\{ e^{i(\zeta s - \bar{\zeta} s')} |M|^2 - e^{i\zeta(s+s')} M^2 \right\} \\ &= 4K_0 e^{-\alpha(s+s')} \frac{\alpha^2}{\rho^2} \{ (\lambda^2 + \mu^2) \cos \alpha(s-s') \\ &\quad - (\lambda^2 - \mu^2) \cos \alpha(s+s') + 2\lambda\mu \sin \alpha(s+s') \} \\ &= 4K_0 e^{-\alpha(s+s')} \frac{\alpha^2}{\rho^2} \{ 2[2\rho - e(1 + \rho)] \cos \alpha(s-s') \\ &\quad - [1 - \rho^2 + 2e(\rho - 1)] \cos \alpha(s+s') \\ &\quad + [2e(1 + \rho) + (\rho - 1)^2 - 4\rho] \sin \alpha(s+s') \}. \end{aligned} \right\} \tag{4.20}$$

Note that

$$L(s, s') = -\frac{\partial}{\partial s} G(s, s') - \frac{\partial}{\partial s'} G(s, s'). \tag{4.21}$$

As for the minimum free energy given by (4.15), we can also express the rate of dissipation as the quadratic form

$$\left. \begin{aligned} D_m(t) &= K_0 \mathbf{g}^2(t) + 4K_0 \frac{\alpha}{\rho} (m^\top h) \cdot \mathbf{g}(t) + 2 \frac{K_0 \alpha^2}{\rho^2} h^\top \mathbf{B} h, \\ m &= (\mu, \lambda) = (e - \rho, 1 - e) \\ \text{and} \quad \mathbf{B} &= 2 \begin{pmatrix} \mu^2 & \lambda\mu \\ \lambda\mu & \lambda^2 \end{pmatrix} \\ &= \begin{pmatrix} 4\rho + \rho^2 - 1 - 4e\rho & 2e(1 + \rho) + (\rho - 1)^2 - 4\rho \\ 2e(1 + \rho) + (\rho - 1)^2 - 4\rho & 1 - 4e + 4\rho - \rho^2 \end{pmatrix}. \end{aligned} \right\} \tag{4.22}$$

This matrix is positive semi-definite. The full expression for $D_m(t)$, given by (4.20), is not manifestly non-negative. However, the earlier form (4.17) is clearly so.

5. Free energies related to the minimum free energy

We now proceed to derive certain other free energies from the expression for the minimum free energy, using a procedure analogous to that in [15] and chapters 15 and 16 of [11].

Replacing the zero at $\omega = \bar{\eta}$ of $H_-(\omega)$ by the zero η of $H_+(\omega)$ gives another free energy, which we now examine. This is the quantity which we denote by $\psi_1(t)$, related to the factorization of

637 $H(\omega)$ given by

$$\left. \begin{aligned}
 &H(\omega) = H_+^{(1)}(\omega)H_-^{(1)}(\omega), \\
 &H_-^{(1)}(\omega) = H_-(\omega) \frac{\omega - \eta}{\omega - \bar{\eta}} = \sqrt{K_0} \frac{(\omega - \eta)(\omega + \eta)}{(\omega + \zeta)(\omega - \bar{\zeta})} = \sqrt{K_0} \frac{\omega^2 - \eta^2}{(\omega + \zeta)(\omega - \bar{\zeta})} \\
 &\text{and} \quad H_+^{(1)}(\omega) = H_+(\omega) \frac{\omega - \bar{\eta}}{\omega - \eta} = \sqrt{K_0} \frac{(\omega - \bar{\eta})(\omega + \bar{\eta})}{(\omega - \zeta)(\omega + \bar{\zeta})} = \sqrt{K_0} \frac{\omega^2 - \bar{\eta}^2}{(\omega - \zeta)(\omega + \bar{\zeta})}.
 \end{aligned} \right\} \quad (5.1)$$

646 The zeros of $H_+^{(1)}(\omega)$ are no longer only in the upper half of the complex plane, whereas those of
 647 $H_-^{(1)}(\omega) = \bar{H}_+^{(1)}(\omega)$ are no longer only in the lower half.

648 We must have $\psi_1(t) \geq \psi_m(t)$, because the latter is the minimum of the set of free energies
 649 for the material. It follows also from the general property that exchanging zeros in this manner
 650 results in a non-decreasing sequence ([11,14,15], p. 363). Some numerical examples, for discrete
 651 spectrum materials, demonstrating relative magnitudes of free energy functionals resulting from
 652 the exchange of zeros are presented in [18].

653 Instead of (4.5), we have

$$\left. \begin{aligned}
 &H_-^{(1)}(\omega) = \sqrt{K_0} \left[1 + \frac{M_1}{\omega + \zeta} - \frac{M_2}{\omega - \bar{\zeta}} \right], \\
 &H_+^{(1)}(\omega) = \sqrt{K_0} \left[1 - \frac{\bar{M}_2}{\omega - \zeta} + \frac{\bar{M}_1}{\omega + \bar{\zeta}} \right] \\
 &\text{and} \quad M_1 = \frac{(\eta^2 - \zeta^2)}{\zeta + \bar{\zeta}}, \quad M_2 = \frac{(\eta^2 - \bar{\zeta}^2)}{\zeta + \bar{\zeta}}.
 \end{aligned} \right\} \quad (5.2)$$

663 Note that $M_2 \neq \bar{M}_1$, in contrast to the minimum free energy case (4.5). Replacing (4.6), we have

$$\left. \begin{aligned}
 &M_1 = \frac{(\eta^2 - \zeta^2)}{2\alpha} = \frac{\alpha}{\rho} \left[\frac{\beta}{\rho} - 1 + i \left(\frac{e_1}{\rho} - \rho \right) \right], \\
 &M_2 = \frac{(\eta^2 - \bar{\zeta}^2)}{2\alpha} = \frac{\alpha}{\rho} \left[\frac{\beta}{\rho} - 1 + i \left(\frac{e_1}{\rho} + \rho \right) \right] \\
 &\text{and} \quad \beta = \frac{\rho^2 + 1}{2}, \quad e_1 = \sqrt{\beta(2\rho - \beta)},
 \end{aligned} \right\} \quad (5.3)$$

672 where (3.24) has been used. Closing the contour of (3.12)₂ on $\Omega^{(-)}$, and using (4.5), we obtain

$$674 \quad \mathbf{q}(t) = -K_0 \mathbf{g}(t) + 2iK_0 \left[1 + \frac{\bar{M}_2}{2\zeta} - \frac{\bar{M}_1}{\zeta - \bar{\zeta}} \right] M_1 \mathbf{g}_+^t(-\zeta) - 2iK_0 \left[1 - \frac{\bar{M}_2}{\bar{\zeta} - \zeta} + \frac{\bar{M}_1}{2\bar{\zeta}} \right] M_2 \mathbf{g}_+^t(\bar{\zeta}). \quad (5.4)$$

677 Comparing with (3.13), it will be observed that

$$\begin{aligned}
 678 \quad A &= -2iK_0 \left[M_1 + \frac{M_1 \bar{M}_2}{2\zeta} - \frac{|M_1|^2}{\zeta - \bar{\zeta}} \right] \\
 681 \quad &= -2iK_0 \left[\bar{M}_2 - \frac{|M_2|^2}{\zeta - \bar{\zeta}} + \frac{M_1 \bar{M}_2}{2\zeta} \right],
 \end{aligned} \quad (5.5)$$

685 where A is defined in (3.4). Note that (5.5) implies the condition

$$686 \quad M_1 - \frac{|M_1|^2}{\zeta - \bar{\zeta}} = \bar{M}_2 - \frac{|M_2|^2}{\zeta - \bar{\zeta}}, \quad (5.6)$$

689 which, in fact, follows from (5.2)_{4,5}. Equation (5.5)₁ can be confirmed with the help of (5.3).

We deduce from (4.1)₂ and (5.2) that

$$\mathbf{p}_-^t(\omega) = -\sqrt{K_0} \left[M_1 \frac{\mathbf{g}_+^t(-\zeta)}{\omega + \zeta} - M_2 \frac{\mathbf{g}_+^t(\bar{\zeta})}{\omega - \bar{\zeta}} \right], \tag{5.7}$$

by closing the contour on $\Omega^{(-)}$. Using (4.2) and (5.7), $\psi_1(t)$ can be written in the form

$$\psi_1(t) = iK_0 \left\{ \frac{(|M_1|^2 + |M_2|^2)|\mathbf{g}_+^t(-\zeta)|^2}{2i\alpha} - \frac{M_1\bar{M}_2[\mathbf{g}_+^t(-\zeta)]^2}{2\zeta} + \frac{\bar{M}_1M_2[\mathbf{g}_+^t(\bar{\zeta})]^2}{2\bar{\zeta}} \right\}. \tag{5.8}$$

Let us define

$$\left. \begin{aligned} M_1 &= \frac{\alpha}{\rho}(\lambda_1 + i\mu_1), & M_2 &= \frac{\alpha}{\rho}(\lambda_1 + i\mu_2) \\ \lambda_1 &= \frac{\beta}{\rho} - 1 = \frac{(\rho - 1)^2}{2\rho}, & \mu_1 &= \frac{e_1}{\rho} - \rho, & \mu_2 &= \frac{e_1}{\rho} + \rho. \end{aligned} \right\} \tag{5.9}$$

and

Then, $\psi_1(t)$ can be expressed as

$$\left. \begin{aligned} \psi_1(t) &= \frac{1}{2} \int_0^\infty \int_0^\infty \mathbf{g}^t(s) \cdot G_1(s, s') \mathbf{g}^t(s') ds ds' \\ \text{and } G_1(s, s') &= 2K_0 \operatorname{Re} \left\{ e^{i(\zeta s - \bar{\zeta} s')} \frac{|M_1|^2 + |M_2|^2}{2\alpha} - i e^{i\zeta(s+s')} \frac{M_1\bar{M}_2}{\zeta} \right\} \\ &= 2K_0 e^{-\alpha(s+s')} \frac{\alpha}{\rho^2} \left\{ [\lambda_1^2 + \frac{1}{2}(\mu_1^2 + \mu_2^2)] \cos \alpha(s - s') \right. \\ &\quad \left. - \frac{1}{2}[\lambda_1^2 + \mu_1\mu_2 - \lambda_1(\mu_1 - \mu_2)] \cos \alpha(s + s') \right. \\ &\quad \left. + \frac{1}{2}[\lambda_1^2 + \mu_1\mu_2 + \lambda_1(\mu_1 - \mu_2)] \sin \alpha(s + s') \right\} \\ &= 2K_0 e^{-\alpha(s+s')} \frac{\alpha}{\rho^2} \{ (1 + \rho^2) \cos \alpha(s - s') \\ &\quad - (1 - \rho) \cos \alpha(s + s') + \rho(1 - \rho) \sin \alpha(s + s') \}, \end{aligned} \right\} \tag{5.10}$$

in terms of the quantities α , ρ and K_0 defined in (3.4). Following the steps leading to (4.15), we can also express $\psi_1(t)$ as the quadratic form

$$\psi_1(t) = \frac{K_0\alpha}{\rho^2} \mathbf{h}^\top \mathbf{A}_1 \mathbf{h}, \tag{5.11}$$

using the notation of (4.15)₂, where

$$\left. \begin{aligned} \mathbf{A}_1 &= \frac{1}{2} \begin{pmatrix} \Lambda + \Delta(\lambda_1 + \Delta) & \Lambda + \lambda_1\Delta \\ \Lambda + \lambda_1\Delta & 3\Lambda + \Delta(\Delta - \lambda_1) \end{pmatrix} \geq 0 \\ \Lambda &= \lambda_1^2 + \mu_1\mu_2, & \Delta &= \mu_1 - \mu_2. \end{aligned} \right\} \tag{5.12}$$

and

The non-negativity property of the matrix \mathbf{A}_1 can be shown for general values of λ_1 , μ_1 and μ_2 . In the present context

$$\mathbf{A}_1 = \begin{pmatrix} \rho(1 + \rho) & \rho(1 - \rho) \\ \rho(1 - \rho) & \rho^2 - \rho + 2 \end{pmatrix}. \tag{5.13}$$

The rate of dissipation associated with $\psi_1(t)$ is given by the analogue of (4.4) for the factorization (5.1), which, in the light of (5.2), becomes

$$\begin{aligned} D_1(t) &= K_0 |\mathbf{g}(t) - iM_1 \mathbf{g}_+^t(-\zeta) + iM_2 \mathbf{g}_+^t(\bar{\zeta})|^2 \\ &= K_0 \left\{ \mathbf{g}^2(t) - 2 \operatorname{Re} [iM_1 \mathbf{g}_+^t(-\zeta) - iM_2 \mathbf{g}_+^t(\bar{\zeta})] \cdot \mathbf{g}(t) \right. \\ &\quad \left. + (|M_1|^2 + |M_2|^2)|\mathbf{g}_+^t(-\zeta)|^2 - M_1\bar{M}_2[\mathbf{g}_+^t(-\zeta)]^2 - \bar{M}_1M_2[\mathbf{g}_+^t(\bar{\zeta})]^2 \right\}. \end{aligned} \tag{5.14}$$

It is of interest to confirm that the analogue of (4.3)₁ holds for the formulae (5.14). Using (3.14) and (4.7), we see that

$$\begin{aligned} \dot{\psi}_1(t) = & iK_0 \left\{ \frac{|M_1|^2 + |M_2|^2}{2i\alpha} [\mathbf{g}_+^t(\bar{\zeta}) + \mathbf{g}_+^t(-\zeta)] - \frac{M_1 \bar{M}_2 \mathbf{g}_+^t(-\zeta)}{\zeta} + \frac{\bar{M}_1 M_2 \mathbf{g}_+^t(\bar{\zeta})}{\bar{\zeta}} \right\} \cdot \mathbf{g}(t) \\ & - K_0 \left\{ (|M_1|^2 + |M_2|^2) |\mathbf{g}_+^t(-\zeta)|^2 - M_1 \bar{M}_2 [\mathbf{g}_+^t(-\zeta)]^2 - \bar{M}_1 M_2 [\mathbf{g}_+^t(\bar{\zeta})]^2 \right\} \\ = & -\mathbf{q}(t) \cdot \mathbf{g}(t) - D_1(t). \end{aligned} \tag{5.15}$$

The demonstration of (5.15)₂ requires the use of condition (5.6). The observation after (4.18) also applies here. The quantity $D_1(t)$ can be expressed as

$$\begin{aligned} D_1(t) = & K_0 \mathbf{g}^2(t) + 2K_0 \frac{\alpha}{\rho} \mathbf{g}(t) \cdot [(\mu_1 - \mu_2) \mathbf{g}_r^t(\alpha) + 2\lambda_1 \mathbf{g}_i^t(\alpha)] \\ & + \frac{1}{2} \int_0^\infty \int_0^\infty \mathbf{g}^t(s) \cdot L_1(s, s') \mathbf{g}^t(s') ds ds' \\ \text{and} \quad L_1(s, s') = & 2K_0 \operatorname{Re} \left\{ e^{i(\zeta s - \bar{\zeta} s')} (|M_1|^2 + |M_2|^2) - 2 e^{i\zeta(s+s')} M_1 \bar{M}_2 \right\} \\ = & 2K_0 e^{-\alpha(s+s')} \frac{\alpha^2}{\rho^2} \left\{ (2\lambda_1^2 + \mu_1^2 + \mu_2^2) \cos \alpha(s - s') \right. \\ & \left. - 2(\lambda_1^2 + \mu_1 \mu_2) \cos \alpha(s + s') + 2\lambda_1(\mu_1 - \mu_2) \sin \alpha(s + s') \right\} \\ = & 4K_0 e^{-\alpha(s+s')} \frac{\alpha^2}{\rho^2} \left\{ (\rho^2 + 1) \cos \alpha(s - s') \right. \\ & \left. + (\rho^2 - 1) \cos \alpha(s + s') - (\rho - 1)^2 \sin \alpha(s + s') \right\}. \end{aligned} \tag{5.16}$$

Note that

$$L_1(s, s') = -\frac{\partial}{\partial s} G_1(s, s') - \frac{\partial}{\partial s'} G_1(s, s'). \tag{5.17}$$

We can also express the rate of dissipation in a form similar to (4.22)

$$\begin{aligned} D_1(t) = & K_0 \mathbf{g}^2(t) + 2K_0 \frac{\alpha}{\rho} (m^\top h) \cdot \mathbf{g}(t) + 2 \frac{K_0 \alpha^2}{\rho^2} h^\top \mathbf{B}_1 h, \\ m = & (\mu_1 - \mu_2, 2\lambda_1) = \left(-2\rho, 2 \left(\frac{\beta}{\rho} - 1 \right) \right) \\ \text{and} \quad \mathbf{B}_1 = & \frac{1}{2} \begin{pmatrix} (\mu_1 - \mu_2)^2 & 2\lambda_1(\mu_1 - \mu_2) \\ 2\lambda_1(\mu_1 - \mu_2) & 4\lambda_1^2 + (\mu_1 + \mu_2)^2 \end{pmatrix} \\ = & \frac{1}{2} \begin{pmatrix} 4\rho^2 & -2(\rho - 1)^2 \\ -2(\rho - 1)^2 & 4 \end{pmatrix}. \end{aligned} \tag{5.18}$$

This matrix is positive definite. The full expression for $D_1(t)$, given by (5.16), is not manifestly non-negative. However, the earlier form (5.14) is clearly so. From (4.16) and (5.13), we find that

$$\mathbf{A}_1 - \mathbf{A} = \begin{pmatrix} 2e\rho & 2\rho(1 - e) - (\rho - 1)^2 \\ 2\rho(1 - e) - (\rho - 1)^2 & 2e(2 + \rho) - 4e^2 \end{pmatrix}, \tag{5.19}$$

which can be shown to be non-negative.

The other intermediate free energy is obtained by exchanging the other zeros in $H_\pm(\omega)$, so that the factor $(\omega - \eta)/(\omega - \bar{\eta})$ in the second line of (5.1) is replaced by $(\omega + \bar{\eta})/(\omega + \eta)$. The resulting formulae are similar, but with η replaced by $\bar{\eta}$ or e_1 replaced by $(-e_1)$, which follows by virtue of (3.24) and the last relation of (5.3). This actually produces the same free energy, because (5.10) and (5.13) do not depend on the square root quantity e_1 , given in (5.3), but only on its square.

The maximum free energy is obtained by exchanging both zeros in $H_\pm(\omega)$. This amounts to changing the sign of e in the formulae (4.14) and (4.16). The resulting matrix corresponding to \mathbf{A}

in (4.16) is easily shown to be greater than or equal to \mathbf{A} . It can also be shown to be greater than or equal to \mathbf{A}_1 , given by (5.13), using a procedure similar to the demonstration that $\mathbf{A}_1 - \mathbf{A}$ in (5.19) is non-negative.

6. Conclusion

Explicit expressions for the minimum, intermediate and maximum free energies are derived for the second-order approximation of Tzou's generalization of Fourier's law. Tzou's theory and its second-order approximation have finite speeds of heat conduction. When the second-order theory is expressed explicitly as that for a material with memory, it emerges that the kernel consists of an exponential decay factor multiplying trigonometric terms. The latter quantities introduce fluctuating behaviour which means that certain standard functionals are not valid free energies for this material. These are often used for other materials, in part because of their simplicity.

On the other hand, the minimum, maximum and intermediate free energies, originally derived in the context of viscoelasticity, are valid for this material, and indeed for a very wide class of materials with memory. The explicit expressions for these are however somewhat more difficult to derive. The derivations given here were aided by a reasonably close but not a perfect analogy with for example the viscoelastic case. Differences arise as outlined before (3.6) and the last paragraph of §3.

The importance of explicit algebraic forms for free energies is discussed in the Introduction.

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