

## Viscoelastic solids with unbounded relaxation function

C. Giorgi and A. Morro

Linear viscoelastic solids are considered where the relaxation function is unbounded in that the initial value of the function and the derivative may be infinite but the function, freed from the equilibrium modulus, is integrable. The second law is given a general form for approximate cycles and then for cycles. Thermodynamic restrictions are derived in connection with cycles and shown to be equivalent to those obtained for bounded relaxation functions. Then the thermodynamic restrictions are shown to be also sufficient for the validity of the second law in the general case of approximate cycles. Finally, a functional is considered which proves to be endowed with the characteristic properties of the free energy.

### 1 Introduction

The model of linear viscoelastic solids rests upon the constitutive relation

$$\mathbf{T}(t) = \mathbf{G}_0 \mathbf{E}(t) + \int_0^\infty \mathbf{G}'(s) \mathbf{E}(t-s) ds \quad (1.1)$$

where  $\mathbf{T}$  is the Cauchy stress tensor and  $\mathbf{E}$  is the infinitesimal strain tensor. The (fourth-order) tensor  $\mathbf{G}_0$  is called the instantaneous elastic modulus and the tensor function

$$\mathbf{G}(s) = \mathbf{G}_0 + \int_0^s \mathbf{G}'(u) du,$$

on  $\mathbb{R}^+$ , is called relaxation function. It is usually understood that  $\mathbf{G}_0$  and  $\mathbf{G}'_0 = \mathbf{G}'(0)$  are bounded tensors while the Boltzmann function  $\mathbf{G}'$  is absolutely integrable, namely  $\mathbf{G}' \in L^1(\mathbb{R}^+)$ . Yet there are indications that sometimes such boundedness conditions are overly restrictive.

An indication that  $\mathbf{G}'$  may have singularities arose from some rheological models motivated by molecular behaviour [1–3]. This is the case, for instance,

of polymer solutions where macromolecules are modelled as freely-jointed beadrod chains. Another indication came from experimental work of Lann [4] whereby it seems that for certain materials the unboundedness of  $G_0$  and/or  $G'_0$  has to be allowed.

On the mathematical side a great deal of interest has been attracted by the suggestive properties of the solution to the Rayleigh problem. In particular Narain and Joseph [5] have investigated the Rayleigh problem, in the one-dimensional case, in the form of step jumps in the velocity or displacement of the boundary of an incompressible fluid in a shearing motion. They have found that the discontinuity propagates into the interior with a speed  $\sqrt{G_0/\rho}$ ,  $\rho$  being the mass density, if the values  $G_0, G'_0$  are both finite. If  $G_0$  is finite but  $G'_0 = -\infty$ , then the boundary of the support of the solution still propagates with the speed  $\sqrt{G_0/\rho}$ . If  $G_0$  is finite but  $G'_0$  vanishes then the amplitude of the discontinuity turns out to remain constant as it happens in nondissipative bodies. Finally, in the case  $G_0 = \infty$  the fluid shows a parabolic behaviour in that the discontinuity is felt instantaneously throughout the fluid. Quite analogous results have been derived by Narain and Joseph [6] for viscoelastic solids.

In these and similar investigations various assumptions have been considered for the relaxation function. For instance, monotonicity of  $G$  on  $\mathbb{R}^+$  while being an element of a suitable fractional Sobolev space [7] or monotonicity of  $G, G'$  and a proper behaviour of  $G$  at infinity [6]. While such conditions are well motivated by technical reasons, there are indications [8] that they may be too restrictive.

Also from a physical viewpoint, it seems natural to ask about the possible restrictions, on the relaxation function, placed by thermodynamics. For bounded relaxation functions this question has been completely solved in [9], cf. also [10]. In this paper we determine necessary and sufficient conditions, on unbounded relaxation functions, for the validity of the second law. Then we establish the expected connection with the analogous conditions for bounded relaxation functions. Finally we consider a functional which, owing to the thermodynamic restrictions, enjoys the properties of a free energy.

The type of unboundedness we mean and the thermodynamic framework are made precise in the following sections.

## 2 Constitutive model

Consider the viscoelastic solid as described by (1.1) where  $G'$  need not be an element of  $L^1(\mathbb{R}^+)$ . Let  $G_\infty = \lim_{s \rightarrow \infty} G(s)$ . Then it is convenient to introduce  $\tilde{G}(s) = G(s) - G_\infty$  and to express the constitutive equation in terms of  $\tilde{G}$  and  $G_\infty$ . An integration by parts of (1.1) yields

$$T(t) = G_\infty E(t) + \int_0^\infty \tilde{G}(s) \dot{E}(t-s) ds \tag{2.1}$$

where the superposed dot denotes the time derivative. To (2.1) we associate the constitutive assumptions on  $G$

$$\tilde{G} \in L^1(\mathbb{R}^+), \quad G_\infty \text{ bounded.} \tag{2.2}$$

Accordingly, we let both  $G_0$  and  $G'_0$  be unbounded but require that the possible singularity of  $\tilde{G}(s)$  at  $s = 0$  be integrable. Of course, in dealing with solids we have to require that

$$G_\infty > 0 \tag{2.3}$$

namely  $G_\infty$  is positive definite. The strain  $E$  and the stress  $T$  are allowed to depend on the particle (position) under consideration. Such dependence is understood but not written.

The domain of the functional (2.1) is the set of continuous strain histories  $E'$  on  $\mathbb{R}^+$  whose values are elements of  $\text{Sym}$ , the space of symmetric tensors. As usual we let  $E'(s) = E(t-s), E(\cdot)$  being the strain function on  $\mathbb{R}$ . Any history  $E'$  is taken to be differentiable in time.

$$E'(s) = \frac{d}{dt} E'(s)$$

in the distributional sense.

The state of the body, at time  $t$ , is given by the history  $E'$ . The evolution of the body in a time interval  $[t_1, t_2]$  is determined by the process  $P = E$  in that interval;  $P$  may be regarded as piecewise continuous or square integrable. For formal simplicity, usually we let  $[0, d]$  be the domain of the process. For any history  $E^0$ , the application of the process  $P$  results in the history  $E^d$  given by

$$E^d(s) = \begin{cases} E^0(0) + \int_0^{t-s} P(\tau) d\tau, & s \in [0, d] \\ E^0(s-d), & s \in [d, \infty) \end{cases}$$

It is usual to write  $g(E^0, P)$  to denote the state produced by applying the process  $P$  to the initial state  $E^0$ . We say that a process is closed if  $\int_0^d P(\tau) d\tau = 0$ , namely  $E(d) = E(0)$ . To make the pertinent expressions more immediate, henceforth we write  $E$ , rather than  $P$ , for the process.

## 3 Strain histories space and norm

We assume the existence of a positive-valued function  $h \in L^1(\mathbb{R}^+)$ , monotone decreasing, such that

$$|\tilde{G}(\sigma + \tau)| \leq \gamma h(\sigma) h(\tau), \quad \forall \sigma, \tau \in \mathbb{R}^+ \tag{3.1}$$

for a suitable constant  $\gamma$ . Two examples show that the assumption (3.1) is not severely restrictive. First, consider  $\tilde{G}$  such that

$$|\tilde{G}(s)| \leq \frac{\kappa(s)}{(1+s)^{2\alpha}}$$

where  $\alpha > 1$  and  $\kappa$  is bounded on  $\mathbb{R}^+$  and positive-valued. As it must be,  $\check{G} \in L^1(\mathbb{R}^+)$ . Let  $\gamma$  be the maximum of  $\kappa$  on  $\mathbb{R}^+$ . Then

$$\frac{\kappa(\sigma + \tau)}{(1 + \sigma + \tau)^{2\alpha}} \leq \frac{\gamma}{[(\frac{1}{2} + \sigma) + (\frac{1}{2} + \tau)]^{2\alpha}} \leq \frac{\gamma}{[(1 + 2\sigma)(1 + 2\tau)]^\alpha} = \gamma h(\sigma) h(\tau)$$

provided only that we take  $h(s) = (1 + 2s)^{-\alpha}$ . This makes (3.1) to hold. Second, let

$$|\check{G}(s)| \leq \kappa(s) \exp(-\alpha s)$$

where  $\alpha > 0$  and  $\kappa$  is bounded on  $\mathbb{R}^+$  and positive-valued. Letting  $h(s) = \exp(-\alpha s)$  we have

$$\kappa(\sigma + \tau) \exp[-(\sigma + \tau)] \leq \gamma h(\sigma) h(\tau)$$

and then (3.1) holds.

Through the function  $h$ , to any history  $E'$  we associate the norm  $\|E'\|_h$  given by

$$\|E'\|_h^2 = |E'(0)|^2 + \int_0^\infty h(s) |\dot{E}'(s)|^2 ds.$$

Henceforth we confine our attention to the set of histories

$$\mathcal{R} = \{E' : \mathbb{R}^+ \rightarrow \text{Sym}, \|E'\|_h < \infty\}$$

which then is a normed space. Incidentally, constant histories  $E'(s) = E$  belong to  $\mathcal{R}$  and  $\|E'\|_h = |E|$ . The set  $\mathcal{R}$  is the state space.

To each closed process  $\check{E}$ , of duration  $d$ , and strain  $E_0$  we associate a (unique) periodic history  $\mathcal{E}$  on  $\mathbb{R}^+$  defined as

$$\begin{aligned} \mathcal{E}(0) &= E_0, \\ \mathcal{E}(s) &= \dot{E}(s - md), \quad s \in (md, (m + 1)d), \quad m = 0, 1, \dots \end{aligned} \tag{3.2}$$

In words,  $\mathcal{E}$  is obtained by applying infinitely many times the process  $\check{E}$  to the strain  $E_0$ . For later convenience we show two properties of  $\mathcal{E}$ .

I) If  $\check{E}$  is piecewise continuous (and hence bounded,  $|\dot{E}| \leq k$ ) then  $\mathcal{E} \in \mathcal{R}$ . For,

$$\|\mathcal{E}\|_h^2 = |E_0|^2 + \int_0^\infty h(s) |\mathcal{E}(s)|^2 ds \leq |E_0|^2 + k^2 \int_0^\infty h(s) ds < \infty.$$

II) If  $\check{E} \in L^2(0, d)$  then  $\mathcal{E} \in \mathcal{R}$ .

For, by the definition of  $\mathcal{E}$ , the properties of  $h$  and some rearrangement we have

$$\begin{aligned} \|\mathcal{E}\|_h^2 &= |E_0|^2 + \sum_{m=0}^\infty \int_{md}^{(m+1)d} h(s) |\dot{E}(s - md)|^2 ds \\ &= |E_0|^2 + \sum_{m=0}^\infty \int_0^d h(\tau + md) |\dot{E}(\tau)|^2 d\tau \\ &\leq |E_0|^2 + \sum_{m=0}^\infty h(md) \int_0^d |\dot{E}(\tau)|^2 d\tau. \end{aligned}$$

The integral is finite because  $\dot{E} \in L^2(0, d)$  and the series converges because  $h \in L^1(\mathbb{R}^+)$ . Hence  $\|\mathcal{E}\|_h < \infty$ . Accordingly, if  $\check{E}$  is closed and is an element of  $L^2(0, d)$  then, for each strain  $E_0$ , the corresponding periodic history  $\mathcal{E}$  is admissible, that is  $\mathcal{E} \in \mathcal{R}$ .

The properties I and II allow us to say that the results of the present paper hold for both piecewise continuous and square integrable processes.

The constitutive functional (2.1) is continuous in the norm of  $\mathcal{R}$ , which amounts to the requirement of the fading memory principle. For, by (3.1) with  $\tau = 0$  we have  $|\check{G}(s)| < \gamma h(s)$  and then

$$|T(E')| \leq |G_\infty| |E'(0)| + \int_0^\infty \gamma h(s) |\dot{E}'(s)| ds$$

where  $T(E')$  stands for the functional (2.1). By applying the Schwartz inequality,

$$\int_0^\infty h(s) |\dot{E}'(s)| ds \leq \left( \int_0^\infty h(s) ds \right)^{1/2} \left( \int_0^\infty h(s) |\dot{E}'(s)|^2 ds \right)^{1/2}, \tag{3.3}$$

and letting  $H^2 = \int_0^\infty h(s) ds$  we have

$$|T(E')| \leq \max\{|G_\infty|, \gamma H\} \|E'\|_h$$

the maximum being finite because  $h \in L^1(\mathbb{R}^+)$  and  $G_\infty$  is bounded.

#### 4 Approximate cycles and second law

Let  $\check{E}^0$  be a given initial state and  $\check{E} \in L^1(0, d)$  a given process. A pair  $(\check{E}^0, \check{E})$  is called a cycle if  $g(\check{E}^0, \check{E}) = E^0$ . Of course  $E$  must be closed for  $(\check{E}^0, \check{E})$  to be a cycle. In viscoelasticity cycles are quite rare. Then it is important to characterize neighbourhoods of a given state.

Let  $\mathcal{O}_\nu(E')$  stand for the  $\nu$ -neighbourhood of  $E'$  which consists of the histories  $E'$  such that  $\|E' - E'\|_h < \nu$ . A pair  $(E^0, \check{E})$  is called  $\nu$ -approximate cycle if  $\check{E}$  is closed and  $g(E^0, \check{E}) \in \mathcal{O}_\nu(E^0)$ . Since  $\check{E}$  is closed then the initial history  $E^0$  and the final history  $E^d$  have a common value at  $s = 0$ , i.e.,

$E^d(0) = E^0(0)$ . Accordingly  $E^d \in \mathcal{P}_V(E^0)$  means that

$$\int_0^\infty h(s) |E^d(s) - \dot{E}^0(s)|^2 ds < \nu.$$

With these notions we state the second law as follows.

**Second law.** For every  $\varepsilon > 0$  there exists  $\nu_\varepsilon > 0$  such that

$$\int_0^d T(t) \cdot \dot{E}(t) dt > -\varepsilon \tag{4.1}$$

for every  $\nu_\varepsilon$ -approximate cycle  $(E^0, \dot{E})$  in  $[0, d]$ .

The particular case of cycles corresponds to  $\varepsilon = 0$ ,  $\nu_\varepsilon = 0$ . Specifically we can write

**Second law for cycles.** The inequality

$$\int_0^d T(t) \cdot \dot{E}(t) dt > 0 \tag{4.2}$$

holds for any non-constant cycle  $(E^0, \dot{E})$  in  $[0, d]$ .

Of course, if  $E'$  is a constant history then (4.2) is replaced by a trivial equality.

### 5 Thermodynamic restrictions

The constitutive functional (2.1) must comply with the general statement (4.1) of the second law. Meanwhile the statement (4.2) must hold in the particular case of cycles. Then, to begin with we determine some consequences of the second law for cycles. Such consequences involve the half-range Fourier cosine and sine transform of  $\tilde{G}$ . For any real-valued function  $f \in L^1(\mathbb{R}^+)$  we define the half-range Fourier cosine and sine transform  $f_c$  and  $f_s$  as

$$f_c(\omega) = \int_0^\infty f(u) \cos \omega u du, \quad f_s(\omega) = \int_0^\infty f(u) \sin \omega u du, \quad \omega \in \mathbb{R}^+.$$

The Fourier transform  $\tilde{f}$  of  $f \in L^1(\mathbb{R}^+)$  is defined as

$$\tilde{f}(\omega) = \int_0^\infty f(u) \exp(-i\omega u) du.$$

Letting a star \* denote the complex conjugate we have  $f^*(\omega) = \tilde{f}(-\omega)$ . We denote by a superscript  $T$  the transpose of a fourth-order tensor,  $T$  say, such that

$$A \cdot T B = B \cdot T^T A$$

for any pair of symmetric second-order tensors  $A, B$ .

**Theorem 1.** The second law of thermodynamics holds only if

$$G_\infty = G_\infty^T, \tag{5.1}$$

$$\tilde{G}_c(\omega) > 0, \quad \forall \omega \in \mathbb{R}^{++}. \tag{5.2}$$

**Proof.** Letting  $E_1, E_2 \in \text{Sym}$ , consider the periodic tensor function

$$\tilde{E}(t) = E_1 \cos \omega t + E_2 \sin \omega t, \quad \omega \in \mathbb{R}^{++}.$$

For any finite value of  $\omega$  the history  $\tilde{E}'$  is an element of  $\mathcal{H}$ . Since the period is  $2\pi/\omega$ , to fix ideas we let  $d = 2\pi/\omega$ . In view of (2.1), substitution in (4.2) and integration with respect to  $t$  yields

$$E_2 \cdot (G_\infty - G_\infty^T) E_1 + \omega [E_1 \cdot \tilde{G}_c(\omega) E_1 + E_2 \cdot \tilde{G}_c(\omega) E_2 + E_2 \cdot (\tilde{G}_s(\omega) - \tilde{G}_s^T(\omega)) E_1] > 0. \tag{5.3}$$

The limit case  $\omega \rightarrow 0$  and the arbitrariness of  $E_1, E_2$  imply the symmetry of  $G_\infty$ . Accordingly, letting  $E_1 = E_2$  we conclude that  $\tilde{G}_c(\omega)$  must be positive definite for any non-zero, finite  $\omega$ .  $\square$

**Remark.** By (5.3), and (5.1), it follows a condition on  $\tilde{G}$  which is stronger than (5.2). In fact, it simply follows that the formal tensor

$$K = \begin{pmatrix} \tilde{G}_c & \frac{1}{2}(\tilde{G}_s^T - \tilde{G}_s) \\ \frac{1}{2}(\tilde{G}_s^T - \tilde{G}_s) & \tilde{G}_c \end{pmatrix},$$

on pairs of tensors in  $\text{Sym}$ , is positive definite. This means that thermodynamics allows  $\tilde{G}_s^T - \tilde{G}_s$  to be non-zero but forces it to be "smaller" than  $\tilde{G}_c$ . The positive definiteness of  $K$  can also be expressed, in terms of  $\Sigma = i(\tilde{G}_c + i\tilde{G}_s)$  and  $E = E_1 + iE_2$ , by

$$\mathcal{F}[\hat{E}^* \cdot \Sigma \hat{E}] > 0$$

for any non-zero  $\hat{E}$ .

We have just seen that the properties (5.1), (5.2) are necessary conditions for the validity of the second law. Then we can regard the model of viscoelastic solids as being characterized by (2.1), (2.2), (2.3) along with (5.1). Yet the proof of Theorem 1 has shown that really, even in the particular case of time-harmonic histories, the second law leads to the inequality (5.3) which is stronger than (5.1), (5.2) and involves also the half-range Fourier sine transform of  $\tilde{G}$ . It is (5.3) that proves to be sufficient for the validity of the second law.

When the viscoelastic solid is described by the standard relation (1.1), with  $G' \in L^1(\mathbb{R}^+)$ , the thermodynamic restrictions involve the half-range Fourier sine transform  $G'_s$ . Precisely, the thermodynamic restrictions are shown to be expressed by [9]

$$E_1 \cdot (G_0^T - G_0) E_2 - E_1 \cdot G'_s(\omega) E_1 - E_2 \cdot G'_s(\omega) E_2 - E_1 \cdot (G'_c(\omega) - G_c^T(\omega)) E_2 > 0, \quad \forall \omega \in \mathbb{R}^{++}, \tag{5.4}$$

whence

$$G_0 = G_0^T, \tag{5.5}$$

$$G_\infty = G_\infty^T, \tag{5.6}$$

$$G'_i(\omega) < 0, \quad \forall \omega \in \mathbb{R}^{++}. \tag{5.7}$$

Of course (5.4), and then (5.5)–(5.7), are derived in connection with cycles corresponding to time-harmonic evolutions of the strain.

Compatibility of the approach for  $\tilde{G} \in L^1(\mathbb{R}^+)$ , with that for  $G' \in L^1(\mathbb{R}^+)$  requires that the condition (5.3) be equivalent to (5.4), obviously by allowing  $\tilde{G} \in W^{1,1}(\mathbb{R}^+)$ . To show that this is so we make use of the following properties. If  $G \in W^{1,1}(\mathbb{R}^+)$  then

$$\omega \tilde{G}_c(\omega) = -G'_i(\omega), \quad \forall \omega \in \mathbb{R} \tag{5.8}$$

and

$$\omega \tilde{G}_s(\omega) = G_0 - G_\infty + G'_i(\omega) \quad \forall \omega \in \mathbb{R}. \tag{5.9}$$

The proof is immediate. For, since  $G'$  is integrable we can consider  $G'_i(\omega)$ ,  $\omega \in \mathbb{R}$ . An integration by parts gives

$$G'_i(\omega) = \int_0^\infty G'(u) \sin(\omega u) du = -\omega \int_0^\infty [G(u) - G_\infty] \cos \omega u du,$$

namely the property (5.8). Similarly we have

$$G'_c(\omega) = \int_0^\infty G'(u) \cos(\omega u) du = [G(u) - G_\infty] \cos \omega u \Big|_0^\infty + \omega \int_0^\infty [G(u) - G_\infty] \sin \omega u du$$

whence (5.9) follows. An immediate substitution proves the desired equivalence.

### 6 Sufficiency of the thermodynamic restrictions

Back to the model (2.1) it is natural to ask whether (5.1), (5.2), and possibly (5.3), are sufficient for the validity of the second law for approximate cycles. The question is not trivial because (5.3) arises in connection with a particular set of cycles. The sufficiency would mean that, for linear viscoelasticity, all thermodynamic features are contained in the behaviour along cycles and, moreover, that among cycles it is enough to examine time-harmonic evolutions. As a first step we show the following property.

**Theorem 2.** *If  $G$  satisfies (5.3), and hence (5.1)–(5.2), then the inequality (4.2) holds for every periodic history, with period  $d$ .*

**Proof.** Let  $E: \mathbb{R} \rightarrow \text{Sym}$  be periodic with period  $d$ . Then by (5.1) we have

$$\int_0^d \dot{E}(t) \cdot G_\infty E(t) dt = 0.$$

This follows immediately by observing that, by (5.1),

$$\dot{E}(t) \cdot G_\infty E(t) = \frac{d}{dt} \left[ \frac{1}{2} E(t) \cdot G_\infty E(t) \right].$$

Accordingly

$$L := \int_0^d T(t) \cdot \dot{E}(t) dt = \int_0^d \left( \int_0^\infty \tilde{G}(s) E(t-s) ds \right) \cdot \dot{E}(t) dt.$$

Since  $E(\cdot)$  is periodic we can write

$$E(t) = \sum_{k=0}^\infty A_k \cos k\omega t + B_k \sin k\omega t$$

where  $\omega = 2\pi/d$ . Substitution allows the work  $L$ , in  $[0, d]$ , to be written as

$$L = \omega^2 \int_0^d dt \int_0^\infty ds \sum_{k,h=1}^\infty [-A_k \sin k\omega t + B_k \cos k\omega t] \cdot \dot{E}(t)$$

$$+ \tilde{G}(s) [-A_k \sin h\omega t \cos h\omega s + A_k \cos h\omega t \sin h\omega s + B_k \cos h\omega t \cos h\omega s + B_k \sin h\omega t \sin h\omega s].$$

Term by term integration of the double series with respect to  $t$  shows that the only non-zero terms are those with  $h = k$ . Then integration with respect to  $s$  yields

$$L = \pi\omega \sum_{k=1}^\infty [A_k \cdot \tilde{G}_r(k\omega) A_k + B_k \cdot \tilde{G}_c(k\omega) B_k + B_k \cdot (\tilde{G}_r(k\omega) - \tilde{G}_c^T(k\omega)) A_k].$$

In view of (5.3), since not all  $A_k, B_k$  can vanish we conclude that  $L > 0$ .  $\square$

To prove that the second law for approximate cycles holds it is convenient to introduce appropriate strain histories. Given a history  $E^0 \in \mathcal{H}$  and a closed process  $E$  of duration  $d$ , let  $E'$  be the corresponding history at time  $t \in [0, d]$ . We define  $\bar{E}'_n$ ,  $n = 0, 1, 2, \dots$ , in the form

$$\bar{E}'_n(s) = \begin{cases} E'(s), & s \in [0, t), \\ E'(s - md), & s \in [(m-1)d + t, md + t), \\ E'(s - nd), & s \in [nd + t, \infty). \end{cases}$$

Of course,  $\bar{E}'_0 = E'$ .

Let  $\bar{E}_m(\tau) = \bar{E}_m^i(\tau - t)$ . For any  $t \in [0, d]$  we have  $\bar{E}_0(t) = \bar{E}_1(t) = \dots = \bar{E}_m(t)$ . This implies that

$$\bar{E}_{m+1}^i(0) = \bar{E}_m^i(0), \quad m = 0, 1, \dots \tag{6.1}$$

Meanwhile, since  $\bar{E}_{m+1}(\tau) = \bar{E}_m(\tau)$ ,  $\tau \in [-md, d]$ ,  $m = 0, 1, \dots$ , then

$$\bar{E}_{m+1}^i(s) = \bar{E}_m^i(s), \quad s \in [0, t + md], \quad m = 0, 1, \dots \tag{6.2}$$

Moreover, by  $\bar{E}_{m+1}(\tau) = \bar{E}_m(\tau + d)$ ,  $\tau \in (-\infty, -md]$ ,  $m = 0, 1, \dots$ , we have  $\bar{E}_{m+1}^i(s) = \bar{E}_m^i(s - d)$ ,  $s \in [t + md, \infty)$ ,  $m = 0, 1, \dots$  (6.3)

Quite naturally we define the history  $\bar{E}'_\infty$  as

$$\bar{E}'_\infty = \lim_{m \rightarrow \infty} \bar{E}'_m$$

The history  $\bar{E}'_\infty$  is periodic, with period  $d$ , and  $\bar{E}'_\infty^d = \bar{E}'_\infty$ . This means that  $(\bar{E}'_\infty, \bar{E})$  is a cycle.

Observe that

$$\bar{E}'_\infty = \bar{E}'_0 + \sum_{m=0}^{\infty} (\bar{E}'_{m+1} - \bar{E}'_m).$$

Then by the identities  $E' = \bar{E}'_0 - \bar{E}'_\infty + \bar{E}'_\infty$  we have

$$E' = \bar{E}'_\infty - \sum_{m=0}^{\infty} (\bar{E}'_{m+1} - \bar{E}'_m). \tag{6.4}$$

We are now able to show that (5.3) implies the validity of the second law for approximate cycles.

**Theorem 3.** *If  $G$  satisfies (5.3), and hence (5.1)–(5.2), then the second law for approximate cycles holds.*

**Proof.** Consider a  $\nu$ -approximate cycle  $(E^0, \bar{E})$  of duration  $d$ . Let  $E'$  be the corresponding state at time  $t \in [0, d]$ . By (6.4) and the linearity of the stress functional we can write

$$T(E') = T(\bar{E}'_\infty) - \sum_{m=0}^{\infty} T(\bar{E}'_{m+1} - \bar{E}'_m).$$

Then the work  $L$  along the approximate cycle  $(E^0, \bar{E})$  is given by

$$L = L_C - L_A \tag{6.5}$$

where

$$L_C = \int_0^d T(\bar{E}'_\infty) \cdot \dot{\bar{E}}(t) dt, \quad L_A = \sum_{m=0}^{\infty} \int_0^d T(\bar{E}'_{m+1} - \bar{E}'_m) \cdot \dot{\bar{E}}(t) dt.$$

By Theorem 2,  $L_C > 0$  in that it is the work performed along the cycle  $(E^0, \bar{E})$ . By (6.1), the present value  $E'_{m+1}(0) - E'_m(0)$  vanishes and hence

$$L_A = \sum_{m=0}^{\infty} \int_0^d \int_0^\infty \dot{\bar{E}}(t) \cdot \check{G}(s) [\bar{E}'_{m+1}(s) - \bar{E}'_m(s)] ds dt.$$

By (6.2) and (6.3) we have

$$L_A = \sum_{m=0}^{\infty} \int_0^d \int_{md+t}^\infty \dot{\bar{E}}(t) \cdot \check{G}(s) [\bar{E}'_m(s - d) - \bar{E}'_m(s)] ds dt$$

whence, by the definition of  $\bar{E}'_m$ ,

$$L_A = \sum_{m=0}^{\infty} \int_0^d \int_0^\infty \dot{\bar{E}}(t) \cdot \check{G}(s) [\dot{E}'(s - (m + 1)d) - \dot{E}'(s - md)] ds dt.$$

Now observe that

$$\begin{aligned} \dot{E}'(s - (m + 1)d) &= \dot{E}'^d(s - t - md), \\ \dot{E}'(s - md) &= \dot{E}'^0(s - t - md), \end{aligned}$$

for any  $s > md + t$ ,  $t \in [0, d]$ ,  $m = 0, 1, \dots$ . The change of variables  $s \rightarrow \sigma = s - md - t$  and  $t \rightarrow \tau = md + t$  yields

$$L_A = \sum_{m=0}^{\infty} \int_{md}^{(m+1)d} \int_0^\infty \dot{E}(\tau - md) \cdot \check{G}(\sigma + \tau) [\dot{E}'^d(\sigma) - \dot{E}'^0(\sigma)] d\sigma d\tau$$

whence, in terms of  $\mathcal{F}$  (cf. (3.2)),

$$L_A = \int_0^\infty \int_0^\infty \mathcal{F}(\tau) \cdot \check{G}(\sigma + \tau) [\dot{E}'^d(\sigma) - \dot{E}'^0(\sigma)] d\sigma d\tau.$$

Now  $E^d, E^0, \mathcal{F}$  are admissible histories with  $E^d(0) = E^0(0) = \mathcal{F}(0)$ . Then, in view of (3.3),

$$\begin{aligned} |L_A| &\leq \int_0^\infty \int_0^\infty \gamma h(\sigma) |\dot{E}'^d(\sigma) - \dot{E}'^0(\sigma)| h(\tau) |\mathcal{F}(\tau)| d\sigma d\tau \\ &\leq \gamma \|E^d - E^0\|_h (\|\mathcal{F}\|_h^2 - |\mathcal{F}(0)|^2)^{1/2} \int_0^\infty h(s) ds. \end{aligned}$$

Letting  $c = \gamma (\|\mathcal{F}\|_h^2 - |\mathcal{F}(0)|^2)^{1/2} \int_0^\infty h(s) ds$  and using (6.5) we can write

$$L \geq L_C - c \|E^d - E^0\|_h > -c \|E^d - E^0\|_h.$$

Since  $(E^0, \bar{E})$  is a  $\nu$ -approximate cycle then

$$\|E^d - E^0\|_h \leq \nu.$$

Hence, letting  $\varepsilon = \nu c$ , we have

$$L > -\varepsilon.$$

So the second law for approximate cycles holds with  $\nu = \varepsilon/c$ .  $\square$

### 7 Free energy

A functional is now examined, which takes the meaning of free energy, in connection with histories  $\mathbf{E}'$  in  $L^2(\mathbb{R}^+)$  while the values of the function  $\mathbf{E}(t)$  are bounded on  $\mathbb{R}$ . Such a functional is reminiscent of analogous ones considered in [11], § 4, and [12].

Let  $W(\mathbf{E}')$  be the work performed by the stress tensor in connection with the history  $\mathbf{E}'$ , namely

$$W(\mathbf{E}') = \int_{-\infty}^t \mathbf{T}(\mathbf{E}') \cdot \dot{\mathbf{E}}(\tau) d\tau.$$

Consider strain histories on  $\mathbb{R}^+$  associated to functions which are constant up to  $t = 0$ , namely

$$\mathbf{E}'(s) = \mathbf{E}_0, \quad s \geq t;$$

we denote by  $\mathcal{H}_0 \subset \mathcal{H}$  the set of such histories. Correspondingly we have

$$W(\mathbf{E}') = \int_0^t \dot{\mathbf{E}}(\tau) \cdot \left[ \mathbf{G}_\infty \mathbf{E}(\tau) + \int_0^\tau \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}'(s) ds \right] d\tau$$

$$= \frac{1}{2} \mathbf{E}(t) \cdot \mathbf{G}_\infty \mathbf{E}(t) - \frac{1}{2} \mathbf{E}_0 \cdot \mathbf{G}_\infty \mathbf{E}_0 + \int_0^t \dot{\mathbf{E}}(\tau) \cdot \left[ \int_0^\tau \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}'(s) ds \right] d\tau.$$

This suggests that we consider the energy functional

$$\mathcal{F}(\mathbf{E}') := \frac{1}{2} \mathbf{E}_0 \cdot \mathbf{G}_\infty \mathbf{E}_0 + W(\mathbf{E}')$$

$$= \frac{1}{2} \mathbf{E}(t) \cdot \mathbf{G}_\infty \mathbf{E}(t) + \int_0^t \dot{\mathbf{E}}(\tau) \cdot \left[ \int_0^\tau \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}'(s) ds \right] d\tau$$

which is well defined on  $\mathcal{H}_0$ . For formal convenience we take the function  $\mathbf{E}(\tau)$  to be constant after time  $t$ , namely

$$\mathbf{E}(\sigma) = \mathbf{E}(t), \quad \sigma \geq t.$$

Meanwhile we extend the range of  $\tilde{\mathbf{G}}$  to  $\mathbb{R}^-$  by letting

$$\tilde{\mathbf{G}}(s) = 0, \quad s < 0. \tag{7.1}$$

Then we can write

$$\mathcal{F}(\mathbf{E}') := \int_0^t \dot{\mathbf{E}}(\tau) \cdot \left[ \int_0^\tau \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}'(s) ds \right] d\tau = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dot{\mathbf{E}}(\tau) \cdot \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}(\tau - s) ds d\tau.$$

The integral on  $s$  is the convolution of  $\tilde{\mathbf{G}}$  and  $\dot{\mathbf{E}}$ . Hence

$$\int_{-\infty}^{\infty} \tilde{\mathbf{G}}(s) \dot{\mathbf{E}}(\tau - s) ds = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{\mathbf{G}}_r(\omega) \dot{\mathbf{E}}_r(\omega) \exp(i\omega\tau) d\omega.$$

Integration on  $\tau$  yields

$$\mathcal{F}(\mathbf{E}') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \dot{\mathbf{E}}_r^*(\omega) \cdot \tilde{\mathbf{G}}_r(\omega) \dot{\mathbf{E}}_r(\omega) d\omega.$$

Since  $\tilde{\mathbf{G}}_r(\omega) = \tilde{\mathbf{G}}_i(\omega) - i\tilde{\mathbf{G}}_s(\omega)$  and  $\tilde{\mathbf{G}}_i(\omega)$  is odd in  $\omega$  we have

$$\mathcal{F}(\mathbf{E}') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \dot{\mathbf{E}}_r^*(\omega) \cdot \tilde{\mathbf{G}}_s(\omega) \dot{\mathbf{E}}_r(\omega) d\omega.$$

Incidentally, since

$$\dot{\mathbf{E}}_r(\omega) = \int_0^t \dot{\mathbf{E}}(s) \exp(-i\omega s) ds = \exp(-i\omega t) \int_0^t \dot{\mathbf{E}}'(\tau) \exp(i\omega\tau) d\tau$$

$$= \exp(-i\omega t) [\dot{\mathbf{E}}_r'(\omega)]^*$$

we can write

$$\mathcal{F}(\mathbf{E}') = \frac{1}{2\pi} \int_{-\infty}^{\infty} [\dot{\mathbf{E}}_r'(\omega)]^* \cdot \tilde{\mathbf{G}}_s(\omega) [\dot{\mathbf{E}}_r'(\omega)] d\omega,$$

which makes it explicit that  $\mathcal{F}$  is a functional of  $\dot{\mathbf{E}}'$ .

The condition (5.2) makes  $\mathcal{F}$  to be strictly positive for any non-zero function  $\mathbf{E}$ . Then

$$\mathcal{F}(\mathbf{E}') = \frac{1}{2} \mathbf{E}(t) \cdot \mathbf{G}_\infty \mathbf{E}(t) + \mathcal{F}(\mathbf{E}') \geq \frac{1}{2} \mathbf{E}(t) \cdot \mathbf{G}_\infty \mathbf{E}(t).$$

We now show that  $\mathcal{F}$  is endowed with the characteristic properties of the free energy.

Letting  $\phi(\mathbf{E}) = \frac{1}{2} \mathbf{E} \cdot \mathbf{G}_\infty \mathbf{E}$  we can write

$$\mathcal{F}(\mathbf{E}') \geq \phi(\mathbf{E}(t)). \tag{7.2}$$

This means that among the histories ending with the value  $\mathbf{E}(t)$  the constant history  $\mathbf{E}'$  has the minimal value of  $\mathcal{F}$ .

Let  $\bar{\mathbf{T}}(\mathbf{E}) = \mathbf{T}(\mathbf{E}')$  be the value of the functional  $\mathbf{T}(\mathbf{E}')$  when  $\mathbf{E}'(s) = \bar{\mathbf{E}}$ ,  $s \in \mathbb{R}^+$ , namely

$$\bar{\mathbf{T}}(\bar{\mathbf{E}}) = \mathbf{G}_\infty \bar{\mathbf{E}}.$$

It follows immediately that

$$\frac{\partial \phi}{\partial \mathbf{E}}(\bar{\mathbf{E}}) = \bar{\mathbf{T}}(\bar{\mathbf{E}}). \tag{7.3}$$

For any  $t_1, t_2$  in  $(0, t)$ ,  $t_1 < t_2$ , let

$$\begin{aligned} \mathscr{W}_{t_1}^{t_2} &= \int_{t_1}^{t_2} \mathbf{T}(\mathbf{E}^\tau) \cdot \dot{\mathbf{E}}(\tau) \, d\tau \\ &= \int_0^{t_2} \mathbf{T}(\mathbf{E}^\tau) \cdot \dot{\mathbf{E}}(\tau) \, d\tau - \int_0^{t_1} \mathbf{T}(\mathbf{E}^\tau) \cdot \dot{\mathbf{E}}(\tau) \, d\tau. \end{aligned}$$

Hence

$$\mathscr{W}_{t_1}^{t_2}(\mathbf{E}^\tau) = W(\mathbf{E}^{t_2}) - W(\mathbf{E}^{t_1}).$$

We can view  $\mathscr{W}_{t_1}^{t_2}(\mathbf{E}^\tau)$  as the work of the stress  $\mathbf{T}$  in passing from the history  $\mathbf{E}^{t_1}$  to the history  $\mathbf{E}^{t_2}$ . It is immediate to see that

$$\mathcal{F}(\mathbf{E}^{t_2}) - \mathcal{F}(\mathbf{E}^{t_1}) = \mathscr{W}_{t_1}^{t_2}(\mathbf{E}^\tau). \quad (7.4)$$

Two more properties of  $\mathcal{F}$  hold. One property is

$$\mathscr{W}_{t_1}^{t_2}(\mathbf{E}^\tau) \geq \phi(\mathbf{E}(t_2)) - \phi(\mathbf{E}(t_1)), \quad 0 < t_1 < t_2 < t, \quad (7.5)$$

where equality holds if and only if  $\dot{\mathbf{E}}(\tau) = 0$ ,  $\forall \tau \in (t_1, t_2)$ . To show that this is so observe that, by (7.4),

$$\mathscr{W}_{t_1}^{t_2}(\mathbf{E}^\tau) = \frac{1}{2} \mathbf{E}(t_2) \cdot \mathbf{G}_\infty \mathbf{E}(t_2) - \frac{1}{2} \mathbf{E}(t_1) \cdot \mathbf{G}_\infty \mathbf{E}(t_1) + \int_{t_1}^{t_2} \int_0^\tau \dot{\mathbf{E}}(\tau) \cdot \dot{\mathbf{G}}(s) \dot{\mathbf{E}}(\tau - s) \, ds \, d\tau.$$

The integral may be viewed as  $\mathcal{F}$  evaluated in conjunction with functions  $\mathbf{E}(\tau)$  which are constant outside the interval  $[t_1, t_2]$ . Then the integral is positive and (7.5) follows.

The other property is

$$\frac{\partial \mathcal{F}(\mathbf{E}^\tau)}{\partial \mathbf{E}(t)} = \mathbf{T}(\mathbf{E}^\tau) = \mathbf{G}_\infty \mathbf{E}(t) + \int_0^t \dot{\mathbf{G}}(s) \dot{\mathbf{E}}(s) \, ds, \quad t > 0. \quad (7.6)$$

For,

$$\mathcal{F}(\mathbf{E}^\tau) = \frac{1}{2} \mathbf{E}_0 \cdot \mathbf{G}_\infty \mathbf{E}_0 + \int_0^t \mathbf{T}(\mathbf{E}^\tau) \cdot \dot{\mathbf{E}}(\tau) \, d\tau.$$

Upon integrations by parts we have

$$\begin{aligned} \mathcal{F}(\mathbf{E}^\tau) &= \frac{1}{2} \mathbf{E}_0 \cdot \mathbf{G}_\infty \mathbf{E}_0 + [\mathbf{T}(\mathbf{E}^\tau) \cdot \mathbf{E}(\tau)]_0^t - \int_0^t \dot{\mathbf{T}}(\mathbf{E}^\tau) \cdot \mathbf{E}(\tau) \, d\tau \\ &= \mathbf{T}(\mathbf{E}^\tau) \cdot \mathbf{E}(t) - \int_0^t [\mathbf{G}_\infty \dot{\mathbf{E}}(\tau) + \int_{-\infty}^\infty \dot{\mathbf{G}}(\tau - s) \dot{\mathbf{E}}(s) \, ds] \cdot \mathbf{E}(\tau) \, d\tau \\ &= \mathbf{T}(\mathbf{E}^\tau) \cdot \mathbf{E}(t) - \frac{1}{2} (\mathbf{E}(t) - \mathbf{E}_0) \cdot \mathbf{G}_\infty (\mathbf{E}(t) - \mathbf{E}_0) \\ &\quad - \int_0^t \mathbf{E}(\tau) \cdot \int_{-\infty}^\infty \dot{\mathbf{G}}(\tau - s) \dot{\mathbf{E}}(s) \, ds \, d\tau. \end{aligned}$$

The integral is independent of the value  $\mathbf{E}(t)$  and then (7.6) follows.

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C. Giorgi

Dipartimento di Matematica  
Universita' della Calabria  
Cosenza, Italy

A. Morro  
DIBE, Universita'  
Genova, Italy

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