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Free energy and internal variables in linear viscoelasticity

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Fisica. — *Free energy and internal variables in linear viscoelasticity.* Nota di Angelo Morro (*) e Maurizio Vianello (**), presentata (***) dal Corrisp. C. Cercignani.

Abstract. — In connection with the determination of the free energy functional for the viscoelastic stress tensor, a viscoelastic material is considered as described by a material with internal variables. In this framework the free energy is uniquely determined. It proves to be the minimal one in the class of thermodynamically admissible free energies.

Key words: Free energy; Linear viscoelasticity; Internal variables.

Riassunto. — *Energia libera e variabili interne in viscoelasticità lineare.* Nell'ambito del problema della determinazione del funzionale energia per il tensore degli sforzi viscoelastico, si considera un materiale viscoelastico descritto come materiale con variabili interne. In questo schema si individua univocamente l'energia libera che risulta uguale a quella minima nella classe delle energie libere termodinamicamente ammissibili.

1. Introduction.

The problem of the free energy for linearly-viscoelastic materials traces back to Volterra [1]. The subject was reinvestigated by Graffi [2] who showed that the expression given by Volterra satisfies the thermodynamic restrictions derived by Coleman [3] for the free energy of materials with memory. Yet the problem is far from being solved in that there is an intrinsic non-uniqueness in the determination of the free energy even if the thermodynamic restrictions are taken into account (cf. [4]).

Day was the first to elaborate, within his theory of materials with memory, quite a general, operative procedure for determining the explicit expression of a free energy functional [5]. Some remarks on such a procedure are developed elsewhere [6]. Here we observe that Day's definition provides the minimal free energy among those compatible with thermodynamics. Incidentally, for linear viscoelasticity this is just one of the results proved recently by Graffi [7, 8].

Materials with internal variables [9] constitute a model for the description of materials with memory. Day [10] proved that, whenever the dimension of the internal variable space is not greater than that of the observable variable space, then there is an essentially unique entropy.

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Based on such a result, in this note we consider linearly-viscoelastic materials, with relaxation function of exponential type, within the context of materials with internal variables. The aim is twofold. First, to determine the free energy, hopefully unique, of the viscoelastic material. Second, to relate it to the known expressions for the viscoelastic material as a material with fading memory.

2. VISCOELASTIC SOLID WITH INTERNAL VARIABLES.

Consider a body $\mathcal{B}$ occupying a region $\mathcal{R}$ in its reference configuration. All functions considered in this paper depend on the position $X \in \mathcal{R}$ and time $t \in R$.

For the sake of formal simplicity we disregard thermal effects in that we let the body $\mathcal{B}$ be at a uniform and constant temperature. The state of the body is the pair $(\boldsymbol{E}, \boldsymbol{\sigma})$ of the infinitesimal strain tensor $\boldsymbol{E}$ and a tensor $\boldsymbol{\sigma}$ which represents the internal variables. Both $\boldsymbol{E}$ and $\boldsymbol{\sigma}$ have values in Sym, the set of all symmetric tensors. The behaviour of the body is characterized by the response functions

$$T = \tilde{T}(E, \boldsymbol{\sigma}), \qquad \psi = \tilde{\psi}(E, \boldsymbol{\sigma}), \tag{2.1}$$

for the Cauchy stress tensor $\boldsymbol{T}$ and the free energy, per unit mass, ψ. The evolution of $\boldsymbol{\sigma}$ is governed by the first order differential equation

$$\dot{\boldsymbol{\sigma}} = \tilde{\boldsymbol{\sigma}}(E, \boldsymbol{\sigma}), \tag{2.2}$$

a superposed dot denoting the time derivative.

An explicit model of (2.1) and (2.2) is suggested by linear isothermal viscoelasticity. Let $\hat{\boldsymbol{E}}$ and $\hat{\boldsymbol{\sigma}}$ denote the trace-free part of $\boldsymbol{E}$ and $\boldsymbol{\sigma}$. On assuming that $\mathcal{B}$ is isotropic we specify $(2.1)_1$ as [11]

$$T = \beta (\operatorname{tr} E)\, \mathbf{1} + 2\mu \hat{E} + \boldsymbol{\sigma} \tag{2.3}$$

and (2.2) as

$$\dot{\boldsymbol{\sigma}} = -\alpha \boldsymbol{\sigma} \beta_\sigma (\operatorname{tr} E)\, \mathbf{1} - 2\mu_\sigma \hat{E}\,. \tag{2.4}$$

The quantities $\alpha, \beta, \beta_\sigma, \mu, \mu_\sigma$ are supposed to be real constants. Indeed, β and μ can be viewed as the instantaneous bulk and shear elasticities and then we let $\beta, \mu > 0$. Moreover we let $\alpha > 0$.

Incidentally, the integration of (2.4) yields

$$\begin{aligned} \boldsymbol{\sigma}(t) &= \boldsymbol{\sigma}(t_0) \exp[-\alpha(t - t_0) - \\ &\quad - \beta_\sigma \left\{ \int_{t_0}^{t} \exp[-\alpha(t-s)]\, (\operatorname{tr} E(s))\, ds \right\} \mathbf{1} - 2\mu_\sigma \int_{t_0}^{t} \exp[-\alpha(t-s)]\, \hat{E}(s)\, ds, \end{aligned} \tag{2.5}$$

the dependence on X being understood and not written. The limit $t_0 \to -\infty$ provides the model of linear viscoelasticity with an exponential-type relaxation function.

3. THERMODYNAMIC RESTRICTIONS.

The constitutive eqs. (2.1) and (2.2) are required to satisfy the second law of thermodynamics. Here the second law is taken to be expressed by the Clausius-Duhem inequality namely

$$-\rho\dot{\psi} + \boldsymbol{T}\cdot\dot{\boldsymbol{E}} \geq 0,$$

where ρ is the mass density. On the assumption that $\tilde{\psi}$ is of class C^1 and $\tilde{\boldsymbol{T}}$ is continuous, it follows from

$$\left(-\rho\frac{\partial\tilde{\psi}}{\partial \boldsymbol{E}} + \tilde{\boldsymbol{T}}\right)\cdot\dot{\boldsymbol{E}} - \rho\frac{\partial\tilde{\psi}}{\partial\boldsymbol{\sigma}}\cdot\tilde{\boldsymbol{\sigma}} \geq 0,$$

that

(3.1) $$\tilde{\boldsymbol{T}} = \rho\frac{\partial\tilde{\psi}}{\partial \boldsymbol{E}}$$

and

(3.2) $$\frac{\partial\tilde{\psi}}{\partial\boldsymbol{\sigma}}\cdot\tilde{\boldsymbol{\sigma}} \leq 0.$$

As a result, the functions $\tilde{\boldsymbol{T}}, \tilde{\psi}$ and $\tilde{\boldsymbol{\sigma}}$ are compatible with thermodynamics if and only if they satisfy (3.1) and (3.2).

We now apply (3.1) and (3.2) to the functions (2.3) and (2.4). Since ρ is regarded as constant it is convenient to consider the free energy per unit volume $\Psi = \rho\psi$. By (3.1) and (2.3) we have

(3.3) $$\Psi = \frac{1}{2}\beta(\mathrm{tr}\,\boldsymbol{E})^2 + \mu\hat{\boldsymbol{E}}\cdot\hat{\boldsymbol{E}} + \frac{1}{3}(\mathrm{tr}\,\boldsymbol{E})(\mathrm{tr}\,\boldsymbol{\sigma}) + \hat{\boldsymbol{E}}\cdot\hat{\boldsymbol{\sigma}} + \Psi^*(\boldsymbol{\sigma}),$$

where Ψ^* is an arbitrary function on Sym. Restrictions on Ψ^* are placed by (3.2). In view of (2.4) substitution gives

(3.4) $$\left[\frac{1}{3}(\mathrm{tr}\,\boldsymbol{E})\,\mathbf{1} + \hat{\boldsymbol{E}} + \frac{\partial\Psi^*}{\partial\boldsymbol{\sigma}}\right]\cdot\left[\alpha\frac{1}{3}(\mathrm{tr}\,\boldsymbol{\sigma})\,\mathbf{1} + \alpha\hat{\boldsymbol{\sigma}} + \beta_\sigma(\mathrm{tr}\,\boldsymbol{E})\,\mathbf{1} + 2\mu_\sigma\hat{\boldsymbol{E}}\right] \geq 0.$$

The exploitation of (3.4) is based on the following

LEMMA (1). *Let* $\boldsymbol{A}, \boldsymbol{B} \in \mathrm{Sym}$, *with* $\mathrm{tr}\,\boldsymbol{A} = \mathrm{tr}\,\boldsymbol{B} = 0$, $\boldsymbol{F} \in C^1(\mathrm{Sym}, \mathrm{Sym})$, $a, b \in R$ *and*

$$\Phi(a, b, \boldsymbol{A}, \boldsymbol{B}) := [a\mathbf{1} + \boldsymbol{A} + \boldsymbol{F}(b\mathbf{1} + \boldsymbol{B})]\cdot[b\mathbf{1} + \boldsymbol{B} + \gamma a\mathbf{1} + \nu\boldsymbol{A}], \qquad \gamma, \nu \in R.$$

Then $\Phi \geq 0$ *for arbitrary values of* a, b *and* $\boldsymbol{A}$, $\boldsymbol{B}$ *only if*

(3.5) $$\boldsymbol{F}(b\mathbf{1} + \boldsymbol{B}) = \frac{b}{\gamma}\mathbf{1} + \frac{1}{\nu}\boldsymbol{B}.$$

PROOF. Observe that Φ is minimal at $b = -\gamma a$, $\boldsymbol{B} = -\nu\boldsymbol{A}$. Then $\partial\Phi/\partial(b\mathbf{1} + \boldsymbol{B})$ must vanish whenever $b = -\gamma a$ and $\boldsymbol{B} = -\nu\boldsymbol{A}$. This condition gives

$$a\mathbf{1} + \boldsymbol{A} + \boldsymbol{F}(b\mathbf{1} + \boldsymbol{B}) = 0 \qquad \text{whenever} \qquad b = -\gamma a, \quad \boldsymbol{B} = -\nu\boldsymbol{A}$$

whence (3.5). □

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(1) This lemma generalizes a result obtained by E. Dunn and A. Morro during a conversation in Galway, March 1988.

Substitution from (3.5) yields

$$\Phi(a, b, A, B) = 3\gamma\left(a + \frac{1}{\gamma}b\right)^2 + \nu\left(A + \frac{1}{\nu}B\right)^2$$

and hence $\Phi \geq 0$ if and only if γ, $\nu > 0$.

The exploitation of (3.4) is immediate once we make the identifications

$$a = \frac{1}{3}\operatorname{tr}\boldsymbol{E}, \quad A = \hat{\boldsymbol{E}}, \quad b = \frac{1}{3}\operatorname{tr}\boldsymbol{\sigma}, \quad B = \hat{\boldsymbol{\sigma}}, \quad \gamma = 3\frac{\beta_\sigma}{\alpha}, \quad \nu = 2\frac{\mu_\sigma}{\alpha}.$$

We get

$$\frac{\partial \Psi^*}{\partial \boldsymbol{\sigma}} = \frac{\alpha}{9\beta_\sigma}(\operatorname{tr}\boldsymbol{\sigma})\,\mathbf{1} + \frac{\alpha}{2\mu_\sigma}\hat{\boldsymbol{\sigma}}, \tag{3.6}$$

$$\beta_\sigma > 0, \qquad \mu_\sigma > 0. \tag{3.7}$$

4. Free energy.

Integration of (3.6) gives

$$\Psi^* = \frac{1}{2}\left[\frac{\alpha}{9\beta_\sigma}(\operatorname{tr}\boldsymbol{\sigma})^2 + \frac{\alpha}{2\mu_\sigma}\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{\sigma}}\right].$$

Substitution into (3.3) and some rearrangement yield

$$\Psi = \frac{1}{2}\left(\beta - \frac{\beta_\sigma}{\alpha}\right)(\operatorname{tr}\boldsymbol{E})^2 + \left(\mu - \frac{\mu_\sigma}{\alpha}\right)\hat{\boldsymbol{E}}\cdot\hat{\boldsymbol{E}} + \frac{\beta_\sigma}{2\alpha}\left(\operatorname{tr}\boldsymbol{E} + \frac{\alpha}{3\beta_\sigma}\operatorname{tr}\boldsymbol{\sigma}\right)^2 + \frac{\mu_\sigma}{\alpha}\left(\hat{\boldsymbol{E}} + \frac{\alpha}{2\mu_\sigma}\hat{\boldsymbol{\sigma}}\right)^2. \tag{4.1}$$

We have thus determined explicitly the expression of the free energy.

As it must be, (4.1) complies with a general property of materials with internal variables [9]. By (2.4) each strain $\boldsymbol{E} = 1/3\,(\operatorname{tr}\boldsymbol{E})\,\mathbf{1} + \hat{\boldsymbol{E}}$ corresponds to an equilibrium state with

$$\operatorname{tr}\boldsymbol{\sigma} = -\frac{3\beta_\sigma}{\alpha}\operatorname{tr}\boldsymbol{E}, \qquad \hat{\boldsymbol{\sigma}} = -\frac{2\mu_\sigma}{\alpha}\hat{\boldsymbol{E}}.$$

Then, by (3.7), for each strain $\boldsymbol{E}$ the function $\Psi(\boldsymbol{E}, \boldsymbol{\sigma})$ has a strict minimum at the equilibrium state.

5. Comparison with known free energy functionals.

Following Graffi [7, 8] we denote by Ψ_g the expression of the free energy due to Volterra (and Graffi himself) and by Ψ_d that determined by Day. By (2.3) and (2.5) we have

$$\boldsymbol{T}(t) = \beta(\operatorname{tr}\boldsymbol{E})\,\mathbf{1} - \beta_\sigma\int_{-\infty}^{t}\exp[-\alpha(t-s)]\operatorname{tr}\boldsymbol{E}(s)\,ds\,\mathbf{1} + \\ + 2\mu\hat{\boldsymbol{E}} - 2\mu_\sigma\int_{-\infty}^{t}\exp[-\alpha(t-s)]\,\hat{\boldsymbol{E}}(s)\,ds.$$

Hence we can write Ψ_g and Ψ_d as

$$\Psi_g(t) = \frac{1}{2}\left(\beta - \frac{\beta_\sigma}{\alpha}\right)(\operatorname{tr}\boldsymbol{E}(t))^2 + \left(\mu - \frac{\mu_\sigma}{\alpha}\right)\hat{\boldsymbol{E}}(t)\cdot\hat{\boldsymbol{E}}(t) + \frac{1}{2}\beta_\sigma\int_{-\infty}^{t}\exp[-\alpha(t-s)]\cdot \\ \cdot[\operatorname{tr}\boldsymbol{E}(t) - \operatorname{tr}\boldsymbol{E}(s)]^2\,ds + \mu_\sigma\int_{-\infty}^{t}\exp[-\alpha(t-s)][\hat{\boldsymbol{E}}(t) - \hat{\boldsymbol{E}}(s)]^2\,ds$$

and

$$\Psi_d(t) = \frac{1}{2}\left(\beta - \frac{\beta_\sigma}{\alpha}\right)(\mathrm{tr}\,\boldsymbol{E}(t))^2 + \left(\mu - \frac{\mu_\sigma}{\alpha}\right)\hat{\boldsymbol{E}}(t)\cdot\hat{\boldsymbol{E}}(t) + \frac{\beta_\sigma}{2\alpha}\left\{\mathrm{tr}\,\boldsymbol{E}(t) - \right.$$

$$\left. - \alpha\int_{-\infty}^{t}\exp[-\alpha(t-s)]\,\mathrm{tr}\boldsymbol{E}(s)\,ds\right\}^2 + \frac{\mu_\sigma}{\alpha}\left\{\hat{\boldsymbol{E}}(t) - \alpha\int_{-\infty}^{t}\exp[-\alpha(t-s)]\,\hat{\boldsymbol{E}}(s)\,ds\right\}^2 .$$

It follows at once that our result (4.1) coincides with Day's free energy Ψ_d. What is more, we could never arrive at an expression like Ψ_g on the basis of the internal variable model in that no internal variable term can provide $\boldsymbol{E}(t) - \boldsymbol{E}(s)$.

By applying the Schwarz inequality and assuming the monotone-decreasing property of the relaxation function (2), Graffi [7] proved that $\Psi_d \leq \Psi_g$. This result can also be derived as a consequence of the minimal property of Ψ_d as shown in [6].

It is worth emphasizing that this note involves exponential-type relaxation functions. An analogous investigation for any type of relaxation function is now under way.

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(2) Here expressed by (3.7).

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