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Thermodynamic functions for ageing viscoelasticity: integral form without internal variables

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Abstract

Viscoelastic materials whose creep and relaxation functions depend on the age at loading are considered. First the material is assumed to follow the solidification theory, which explains ageing of concrete by gradual deposition of layers of newly solidified non-ageing viscoelastic constituent (cement gel) on the pore walls. It is shown that the well-known classical Staverman and Schwarzl's and Mandel's formulae for the densities of Helmholtz free energy, free enthalpy and dissipation in a non-ageing viscoelastic material can be generalized to the case of ageing by double Stieltjes integrals over the strain or stress histories. Their integrands contain only the relaxation or compliance functions and their rates, but not the internal variables nor the properties of constituents. The expressions obtained for the free energy and free enthalpy are subsequently shown to possess in general (without restriction to the solidification theory) the property of a potential for the stress or strain, respectively. Consequently, if one formulates three-dimensional expressions for the free energy or free enthalpy on the basis of the solidification theory, one may, conversely, obtain constitutive equations for ageing viscoelasticity that are consistent with continuum thermodynamics. An expression for the dissipated power of an ageing material is also derived. The results should prove useful for approximate solutions, bounds on structural response, and numerical solution algorithms. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The thermodynamic density functions in continuum mechanics are useful for formulating restrictions on positive energy dissipation, revealing certain symmetries with respect to different variables, establishing approximate bounds on some stiffness and compliance characteristics in heterogeneous materials or structures, determining numerical stability restrictions for computational algorithms, etc. In viscoelasticity, formulation of continuum thermodynamics is made difficult by the fact that

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one treats a material that is not in an equilibrium state. This aspect has generated continuing controversy, which can however be resolved by various ways, e.g., on the basis of Coleman's theorems; Coleman (1964), Coleman and Mizel (1964), see also Kestin (1974, 1979, 1992), Day (1972) and Huet (1979, 1982). For linear viscoelasticity without ageing, the basic thermodynamic framework was developed mainly by Staverman and Schwarzl (1952a, b), Biot (1954), Mandel (1964, 1966) and Valanis (1971, 1983), starting from the internal variable viewpoint, and by Coleman (1964), Brun (1965, 1967, 1969), Christensen (1969, 1982) and Truesdell (1969), starting from the macroscopic variable viewpoint.

In this study, attention is focused on viscoelasticity with ageing, manifested by a change of viscoelastic properties as a function of time (rather than strain, damage, load cycles and similar sources). Such ageing, for example, arises in Portland cement concretes due to the long-term chemical reactions of hydration of tri-calcium silicate as well as relaxation of hygro-chemically induced self-equilibrated prestress of the microstructure (Bažant et al., 1997a, b). It causes that the creep or relaxation properties at the ages of one day, one week, one month, one year and ten years are all rather different.

The thermodynamic functions of an ageing viscoelastic material, having the property that their differentiation provides the stress or strain history, have been formulated in Bažant (1979, also partly 1972b, 1975). However, the formulation was in terms of internal variables (partial strains or partial stresses of the Kelvin or Maxwell chain model), which are not as useful as the measurable (external) state variables (strains and stresses) and cannot be determined in a unique way from purely mechanical experiments. The knowledge of internal variables, by contrast, makes it possible to determine the overall properties, which is the basis of the so-called integrated micromechanics as recently developed by Huet (1993b, 1997).

The purpose of this work is to formulate the thermodynamic functions, particularly the densities of the free energy, free enthalpy and energy dissipation rate (or dissipated power), in an integral form in which no internal variables are used. This is the property of the celebrated Staverman and Schwarzl (1952a, b) formula for non-ageing viscoelastic materials. We will attempt to extend this formula to the case of ageing. This problem was recently pointed out as an important pending problem by Huet (1993a), who discussed it on the basis of Fréchet's (1910) integral-type formulation of linear functionals and proposed two particular forms of the free energy functional, each of them being endowed with the property of a potential for materials with instantaneous elasticity. This paper will present a new form of the free energy functional that is valid in general within the framework of the solidification theory (for materials exhibiting instantaneous elasticity) and exhibits the property of a potential for stress. This form can be directly derived from microscopic considerations based on the solidification theory, which was developed for concrete in Bažant (1977) and was extended in Bažant and Prasannan (1989a, b) and Carol and Bažant (1993). However, after deducing from this theory the expressions for the thermodynamic functions, we will show that they may have a more general validity, not restricted to the solidification theory nor to concrete.

2. Staverman–Schwarzl and Mandel formulae for thermodynamics of non-ageing viscoelastic materials

In non-ageing viscoelasticity, the one-dimensional stress–strain relation for uniaxial stress $\sigma(t)$ is written as

$$\sigma(t) = \int_{0^-}^{t} \Psi(t-\xi)\,\mathrm{d}\varepsilon(\xi), \quad \varepsilon(t) = \int_{0^-}^{t} \Phi(t-\xi)\,\mathrm{d}\sigma(\xi) \tag{1}$$

in which ε = strain, $\Phi(t)$ = compliance function, $\Psi(t)$ = relaxation function, and the integrals are Stieltjes integrals [if the derivative $\dot{\varepsilon}(\xi)$ exists (no jumps), they can be transformed to the usual, Riemann integrals by setting $\mathrm{d}\varepsilon(\xi) = \dot{\varepsilon}(\xi)\,\mathrm{d}\xi$]. The minus label at the lower limit of the integral, 0^-, indicates that the integration must begin just before $t = 0$, which is necessary when the loading starts at time $t = 0$ with a jump. The density of the isothermal Helmholtz free energy in the material may be expressed according to the Staverman–Schwarzl formula as follows:

$$\mathscr{F}(t) = \frac{1}{2}\int_{0^-}^{t}\int_{0^-}^{t} \Psi(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{2}$$

An instructive way to derive this relation is to consider the approximation of the relaxation function Ψ according to the Maxwell chain model (Fig. 1), for which $\sigma(t) = \Sigma_{k=1}^{n}\,\sigma_k(t)$, $\dot{\varepsilon} = (\dot{\sigma}_k/E_k) + (\sigma_k/\eta_k)$, $k = 1, 2, \ldots, n$. Here σ_k are the partial stresses of the chain (internal variables), E_k are the elastic moduli, and η_k are the viscosities of the individual Maxwell units. For the Maxwell chain (with relaxation times $\tau_k = \eta_k/E_k$), one has

$$\Psi(t-\xi) = \sum_{k=1}^{n} E_k\,\mathrm{e}^{-\frac{t-\xi}{\tau_k}} \tag{3}$$

The Helmholtz free energy per unit volume of the material may be expressed as a sum of the energies of all the springs of the Maxwell chain at time t;

$$\mathscr{F}(t) = \sum_{k=1}^{n} \frac{\sigma_k^2(t)}{2E_k} \tag{4}$$

Noting that $\sigma_k(t) = \int_0^t E_k \exp\left[-(t-\xi)/\tau_k\right]\mathrm{d}\varepsilon(\xi)$, one gets

$$\mathscr{F}(t) = \sum_k \frac{1}{2E_k}\left(\int_{0^-}^{t} E_k\,\mathrm{e}^{-\frac{t-\xi}{\tau_k}}\,\mathrm{d}\varepsilon(\xi)\right)\left(\int_{0^-}^{t} E_k\,\mathrm{e}^{-\frac{t-\eta}{\tau_k}}\,\mathrm{d}\varepsilon(\eta)\right) \tag{5}$$

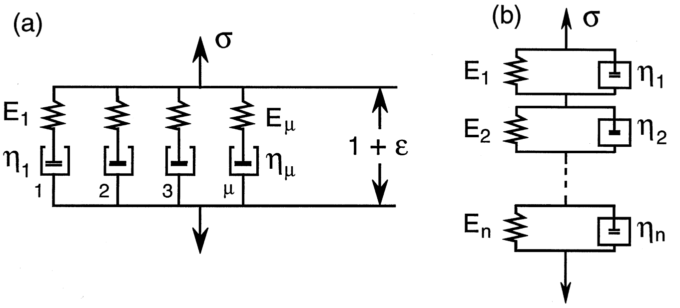

Fig. 1. (a) Maxwell chain model and (b) Kelvin chain model for linear viscoelasticity.

$$= \frac{1}{2}\int_{0^-}^{t}\int_{0^-}^{t}\left(\sum_k E_k\,\mathrm{e}^{-\frac{2t-\xi-\eta}{\tau_k}}\right)\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{6}$$

Here the last expression in parentheses is readily recognized to be equal to the relaxation function of the argument $2t-\xi-\eta$. This proves the last expression to be equivalent to (2).

Lest one might think that the foregoing proof might be restricted to one particular rheological model, note that any linear viscoelastic behavior can be described by the Maxwell chain model or the Kelvin chain model as closely as desired. So the Maxwell chain model is equivalent to the Kelvin chain model or any other model consisting of springs and dashpots, and even to more general models as explained later. This was proven by Roscoe (1950), Staverman and Schwarzl (1952b) and Biot (1954); see also Mandel (1966).

The density $\mathscr{D}$ of the dissipated power, henceforth abbreviated as the dissipation, is

$$\mathscr{D}(t) = \sigma(t)\dot{\varepsilon}(t)-\dot{\mathscr{F}}(t) = \sigma(t)\dot{\varepsilon}(t)-\frac{1}{2}\dot{\varepsilon}(t)\int_{0^-}^{t}\Psi(2t-\xi-t)\,\mathrm{d}\varepsilon(\xi)$$

$$-\frac{1}{2}\dot{\varepsilon}(t)\int_{0^-}^{t}\Psi(2t-t-\eta)\,\mathrm{d}\varepsilon(\eta)-\int_{0^-}^{t}\int_{0^-}^{t}\dot{\Psi}(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{7}$$

$$= -\int_{0^-}^{t}\int_{0^-}^{t}\dot{\Psi}(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{8}$$

where the superior dot denotes the derivatives with respect to the time variable t. This expression can of course, be also obtained by summing the viscous work rates in all the dashpots.

By similar calculations, one can verify that for materials exhibiting instantaneous elasticity (which is not the case, e.g., for the Kelvin unit):

$$\frac{\partial\mathscr{F}(t)}{\partial\varepsilon(t)} = \sigma(t) \tag{9}$$

This shows that, for such materials, $\mathscr{F}$ is indeed a potential for the stress.

For creep under constant stress σ^0, Staverman and Schwarzl gave also the expression of the free energy density of the Maxwell chain in terms of the compliance function $\Phi(t)$. In the present notation, this expression may be written as

$$\mathscr{F}(t) = [\Phi(t)-\tfrac{1}{2}\Phi(2t)]\sigma^0\sigma^0 \tag{10}$$

Using integration by parts in (2), Mandel (1966) extended this expression to general histories in the following form:

$$\mathscr{F}(t) = \frac{1}{2}\int_{0^-}^{t}\int_{0^-}^{t}[2\Phi(t-\xi)-\Phi(2t-\xi-\eta)]\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \tag{11}$$

$$= \sigma(t)\varepsilon(t)-\frac{1}{2}\int_{0^-}^{t}\int_{0^-}^{t}\Phi(2t-\xi-\eta)\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \tag{12}$$

The complementary energy density $\mathscr{F}^*$ (or the negative of the Gibbs free energy density) is defined as the Legendre transform of the free energy, i.e.

$$\mathscr{F}^*(t) = \sigma(t)\varepsilon(t) - \mathscr{F}(t) \tag{13}$$

Substituting (12), one gets

$$\mathscr{F}^*(t) = \frac{1}{2}\int_{0^-}^{t}\int_{0^-}^{t} \Phi(2t-\xi-\eta)\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \tag{14}$$

The dissipation is found to be given as

$$\mathscr{D}(t) = \int_{0^-}^{t}\int_{0^-}^{t} \dot{\Phi}(2t-\xi-\eta)\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \tag{15}$$

As shown in Mandel (1966) and, with a new proof, by Huet (1992), these forms of thermodynamic functions are not restricted to a Maxwell chain, and not even to any particular rheological (spring–dashpot) model. They hold true for internal variables of any kind provided the associated rate equations are first-order differential equations with constant coefficients. Huet's new proof, in particular, shows that, for such internal variables, the kernel with two arguments appearing in the quadratic term of the Fréchet (1910) expression for the free energy should degenerate in a function of the sum of its arguments, a property that is verified here. This result was obtained using the two-dimensional symbolic calculus already applied to nonlinear viscoelasticity by Huet (1973, 1985).

3. Viscoelasticity with ageing

In the case of ageing, the classical linear viscoelastic equations relating the histories of strain ε and uniaxial stress σ read in Volterra–Stieltjes form (Volterra, 1887, 1959) as follows:

$$\varepsilon(t) = \int_{0}^{t} J(t,t')\,\mathrm{d}\sigma(t'), \quad \sigma(t) = \int_{0}^{t} R(t,t')\,\mathrm{d}\varepsilon(t') \tag{16}$$

Here $J(t,t')$ = compliance function for uniaxial stress, i.e., the strain at age t caused by a unit constant uniaxial stress applied at age $t' \leqslant t$, and $R(t,t')$ = relaxation function for uniaxial stress, i.e. the uniaxial stress at age t caused by a unit constant strain applied at age $t' \leqslant t$; $t = 0$ denotes the instant when the solid is first formed, e.g., when the concrete mix sets (changes from fluid to solid). These functions now depend separately on t and t', rather than just on the time lag $t-t'$. The functions $R(t,t_0)$ and $J(t,t')$ are related by a Volterra integral equation of the second kind with parameter t_0, which is known to always have, for a fixed t_0, a unique solution. Unlike non-ageing viscoelasticity, the lower limit of the time integral in (16) need not be written as 0^- because a jump of stress or strain at $t = 0$ is physically impossible; $t = 0$ is the moment at which the material begins to harden and thus cannot sustain a finite shear stress as yet. Equation (16) extends Boltzmann's (1874) superposition principle to linear viscoelastic materials with ageing.

The linear viscoelastic stress–strain relation with ageing was set into operator form by Mandel (1957, 1974a) (whose work was extended to matrix and tensor integro-differential operators by

Huet, 1974). These operators, which are non-commutative, have been applied to the drying of moist clays (Huet, 1970b) and to composite structures (Huet 1970a, 1980). The corresponding numerical aspects have been handled by means of an improved version of the numerical algorithm initially developed by Bažant (1972a).

As emphasized by Huet (1993), an important aspect that has been missing is the corresponding thermodynamic formalism, which would generalize the classical formalism established for the elastic case and for the viscoelastic case without ageing. The present paper aims at filling this gap, exploiting at first for physical insight the solidification theory of Bažant (1977); see also Bažant and Prasannan (1989a, b), Carol and Bažant (1993), and Bažant et al. (1997a, b). The validity of the solidification model and its application to concrete was justified in these works, and so it need not be discussed here. After recalling the main features of this model, we simply derive from a continuum thermodynamics view the consequences of the assumptions underlying this model. Then we study the inverse problem showing that the free energy expression deduced from the solidification model has the property of a potential.

4. Basic concepts of solidification theory

In the initial development of the solidification theory, the objective was to obtain a physically reasonable form of functions J and R characterizing the age dependence of material properties in a manner that does not imply the properties of the constituents of the material to change with time. The ageing can in fact be caused by a change of concentrations of the constituents. The best paradigm is the growth of the mass of cement hydration products per unit volume of Portland cement concrete, which appears to be the main (albeit not the sole) physical mechanism for ageing of the time-hardening type exhibited by this complex material. In this solidification process, the solid hydration products gradually fill the pore space originally occupied by water and by the part of the anhydrous cement that has been dissolved. At temperatures below 100°, the effect of this solidification process on the overall material stiffness prevails over the effect of dissolution of the anhydrous cement grains during hydration. The mathematical consequences of this mechanism of age dependence of creep are captured by the solidification theory (Bažant, 1977; Bažant and Prasannan, 1989a, b; Carol and Bažant, 1993).

It may be noted that there exist other possible ageing mechanisms such as the growth of microcracking and microcrack healing, as well as bonding or debonding within the solid skeleton (for hardened cement gel suggested by Bažant and Prasannan, 1989a). However, they do not prevail in the hardening stage, and would be incompatible with the linearity of the stress–strain relation in (16), which is experimentally well established for the service stress range of concrete. Such processes may be described by the general theory of heterogeneous materials extended to non-ageing viscoelasticity with damage by Huet (1995a, 1997). There is nevertheless one other ageing mechanism that must be expected to occur in the hardening stage of concrete and is compatible with the aforementioned linearity. It is the relaxation of localized high stress peaks in the microstructure of cement gel, recently described by the microprestress-solidification theory (Bažant et al., 1997a, b). Consideration of this physical mechanism is beyond the scope of this paper.

The layers of cement gel that have already solidified carry a finite stress, s, and thus help to resist

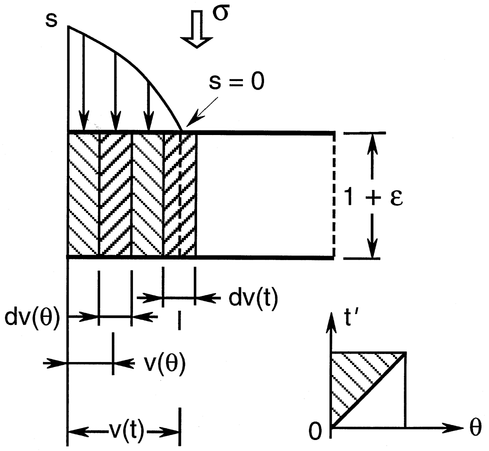

Fig. 2. Model for progressive solidification of layers of non-ageing viscoelastic material from a solution in the pore.

the externally applied load. However, the layers of cement gel are logically considered to be stress-free ($s = 0$) at the moment they solidify. This is an essential feature of the solidification theory proposed by Bažant (1977).

The stress-free initial condition of the freshly solidified constituent layers may be simply captured by the model shown in Fig. 2. In this model (Bažant, 1977), the subsequently deposited layers of the solidified constituent are assumed to be coupled in parallel, subjected to the same macroscopic strain increments $d\varepsilon$, and to carry normal stress parallel to the layers. This strain uniformity assumption is advantageous for keeping the solidification model simple.

5. Mathematical formulation of solidification theory

Let $v(\theta)$ represent the volume of the solidified matter (cement gel or hydration products, in the case of Portland cement concrete) per unit volume of the material at age θ (obviously $0 \leqslant v < 1$). This function, which can be calculated from the initial concentrations of cement and water according to the chemical reaction kinetics and can be determined by fitting experimental data (Bažant and Prasannan, 1989a), is assumed to be given. A layer of infinitesimal volume $dv(\theta)$ is the layer deposited at age θ of the material. In this manner, a one-to-one relationship between the age θ and the layer is introduced. Thus, instead of spatial coordinates, each constituent layer is labeled by the time θ at which it solidified.

The solidifying constituent is considered to be a non-ageing linear viscoelastic material characterized by the compliance function $\Phi(\xi)$ or the associated relaxation function $\Psi(\xi)$, where $\xi = t - t'$ = duration of unit constant stress or strain.

The stress s at age $t > \theta$ in the layer $dv(\theta)$ that solidified at age θ at which the volume of solidified matter within a unit representative volume of the material was $v(\theta)$ may be expressed as:

$$s(\theta, t) = \int_{\theta^-}^{t} \Psi(t-t')\,\mathrm{d}\varepsilon(t') \tag{17}$$

The integration starts just before time θ because a sudden strain jump can occur at time θ at which the non-ageing constituent already exists, having precipitated before. Because the layers of the solidified matter are, in this one-dimensional model, assumed to be mutually coupled in parallel (Fig. 1) and thus subjected to the same strain increment $\mathrm{d}\varepsilon$, the stresses s in all the layers $\mathrm{d}v(\theta)$ are superimposed and must have the macroscopic stress σ as their resultant; i.e.

$$\sigma(t) = \int_{\theta}^{t} s(\theta, t)\,\mathrm{d}v(\theta) \tag{18}$$

In the case of concrete, all the known test results can be described adequately by assuming that there is only one solidification process in which the cement grains are dissolved in water and then solidify from the solution as the hydration product (Bažant and Prasannan, 1989b). But in reality there are several separate chemical processes involved in hydration. So it is of interest to formulate a more general theory involving several separate solidification processes characterized by volume increments $\mathrm{d}v_\mu(\theta)$ ($\mu = 1, \ldots, n$) (obviously $0 \leqslant \Sigma_\mu v_\mu < 0$). In that case, eqns (17) and (18) may be generalized as

$$s_\mu(\theta, t) = \int_{t'=\theta}^{t} \Psi_\mu(t-t')\,\mathrm{d}\varepsilon(t'), \quad \sigma(t) = \sum_{\mu=1}^{n} \int_{\theta=0}^{t} s_\mu(\theta, t)\,\mathrm{d}v_\mu(\theta) \tag{19}$$

where the subscript μ refers to layers of the same constituent μ solidifying at different times, and $\mu = 1, 2, \ldots n$ labels different constituents. Here it is assumed that the layers $\mathrm{d}v_\mu(\theta)$ of the solidified matter for all the separate solidification process (or separate constituents) are subjected to the same macroscopic strain ε.

Substitution of the first equation into the second furnishes:

$$\sigma(t) = \sum_{\mu=1}^{n} \int_{\theta=0}^{t} \int_{t'=0}^{t} \Psi_\mu(t-t')\,\mathrm{d}\varepsilon(t')\,\mathrm{d}v_\mu(\theta) \tag{20}$$

Interchanging the order of integration and taking into account that all Ψ_μ are independent of θ gives

$$\sigma(t) = \sum_{\mu=1}^{n} \int_{t'=0}^{t} \Psi_\mu(t-t') \int_{\theta=0}^{t'} \mathrm{d}v_\mu(\theta)\,\mathrm{d}\varepsilon(t'), \quad \text{or} \quad \sigma(t) = \int_{t'=0}^{t} \sum_{\mu=1}^{n} v_\mu(t')\Psi_\mu(t-t')\,\mathrm{d}\varepsilon(t') \tag{21}$$

This proves that the solidification theory provides a constitutive equation that indeed has the form of (16), with an overall relaxation function of the form

$$R(t, t') = \sum_{\mu=1}^{n} v_\mu(t')\Psi_\mu(t-t') \tag{22}$$

Since Ψ_μ and v_μ cannot be negative, we see that $R(t, t')$ cannot become negative (contrary to what happens in numerical computation of the relaxation function from some models of the creep function with ageing). Furthermore, the last expression automatically satisfies the inequalities:

$$R(t,t') \geqslant 0, \quad \frac{\partial R(t,t')}{\partial t} \leqslant 0, \quad \frac{\partial R(t,t')}{\partial t'} \geqslant 0, \quad \frac{\partial R(t,t')}{\partial t'} \geqslant -\frac{\partial R(t,t')}{\partial t}, \quad \frac{\partial^2 R(t,t')}{\partial t\,\partial t'} \leqslant 0 \tag{23}$$

because

$$v_\mu(t) \geqslant 0, \quad \dot{v}_\mu(t) \geqslant 0 \tag{24}$$

and, for non-ageing viscoelasticity,

$$\Psi_\mu(t) \geqslant 0, \quad \dot{\Psi}_\mu(t) \leqslant 0, \quad \ddot{\Psi}_\mu(t) \geqslant 0 \tag{25}$$

The first and second inequalities in (23) can be deduced from a thermodynamic formulation based on an internal variable framework (Huet, 1992). The third inequality in (23) is implied by the second and the fourth.

Upon replacing t with new variable $t'+\Delta$ and integrating over Δ, one finds the fourth inequality in (23) to be equivalent to the inequalities

$$\left[\frac{\partial R(t'+\Delta,t')}{\partial t'}\right]_{\Delta=\text{const}} \geqslant 0, \quad \text{or } R(t+\Delta,t'+\Delta) \geqslant R(t,t') \quad \text{for } \Delta > 0 \tag{26}$$

These inequalities mean that the material hardens (rather than softens) as it ages.

The last inequality in (23) means that two relaxation curves of ageing material for two different ages t' of initial strain imposition cannot diverge from each other (which is the property of solidification theory and the B3 model, Bažant and Baweja, 1995). A similar non-divergence restriction also applies, in the case of solidification theory, to the compliance function (Bažant and Prasannan, 1989a, b). The non-divergence restriction in (23), however, is dictated by the macroscopic thermodynamic restrictions, that is, the second law of thermodynamics, only in the particular case of the solidification theory, but not in general. There exists an example of an ageing spring–dashpot model (Bažant and Kim, 1978) that does not conform to the solidification theory and violates (23), yet is thermodynamically admissible because the springs and dashpots obey the relations $\dot{\sigma} = E(t)\dot{\varepsilon}$ and $\sigma = \eta(t)\dot{\varepsilon}$ in which $E(t)$ and $\eta(t)$ are positive monotonically increasing functions. However, it is doubtful that such a spring–dashpot model is realistic.

Generalizing the results of Staverman and Schwarzl, and Mandel, we will now derive from the solidification theory the expressions of the thermodynamic functions that correspond to these formulae.

6. Free energy density of solidifying material under uniaxial stress

To formulate thermodynamics of a solidifying material, we now deal with the non-ageing constituents and take into account the variation in their concentrations. Because the solidified constituent itself is not ageing, we may apply to it the Staverman–Schwarzl formula (2). Thus the content of the Helmholtz free energy in layer $\mathrm{d}v_\mu(\theta)$ is

$$\mathscr{F}_{\mu}(\theta,t)\,\mathrm{d}v_{\mu}(\theta)=\left[\frac{1}{2}\int_{\mu=\theta}^{t}\int_{\xi=\theta}^{t}\Psi_{\mu}(2t-\eta-\xi)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta)\right]\mathrm{d}v_{\mu}(\theta) \tag{27}$$

The total Helmholtz free energy of the solidified constituent per unit volume of the material is the sum of the Helmholtz free energies in all the layers, i.e.

$$\mathscr{F}(t)=\sum_{\mu=1}^{n}\int_{\theta=0}^{t}\mathscr{F}_{\mu}(\theta,t)\,\mathrm{d}v_{\mu}(\theta) \tag{28}$$

Substitution of (27) now provides:

$$\mathscr{F}(t)=\frac{1}{2}\int_{\theta=0}^{t}\left[\int_{\eta=\theta}^{t}\int_{\xi=\theta}^{t}\sum_{\mu=1}^{n}\Psi_{\mu}(2t-\eta-\xi)\,\mathrm{d}\varepsilon(\eta)\,\mathrm{d}\varepsilon(\eta)\right]\mathrm{d}v_{\mu}(\theta) \tag{29}$$

Let us now try to reduce the triple integral in this equation to a double integral so as to eliminate the variables v_{μ}. To this end, note first that, due to the symmetry of the kernel Ψ_{μ} with respect to the two variables ξ and η, the non-ageing Staverman–Schwarzl formula in (27) can be written in two equivalent forms corresponding to the partitioning of the square integration domain into two triangles (Fig. 3a and b, respectively);

$$\mathscr{F}_{\mu}(\theta,t)=\int_{\eta=\theta}^{t}\int_{\xi=\eta}^{t}\Psi_{\mu}(2t-\eta-\xi)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{30}$$

$$=\int_{\eta=\theta}^{t}\int_{\xi=\theta}^{\eta}\Psi_{\mu}(2t-\eta-\xi)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{31}$$

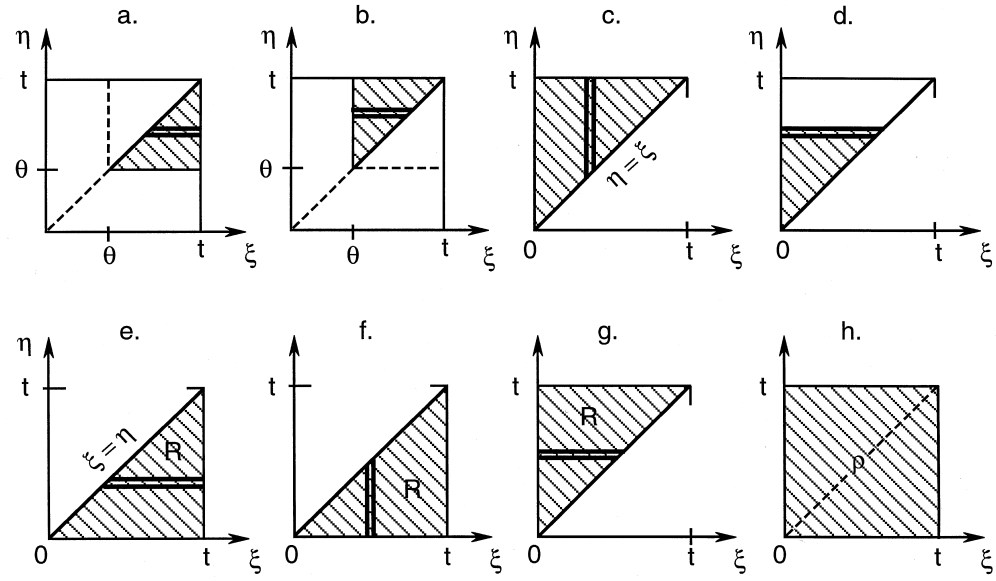

Fig. 3. Various triangular and rectangular integration domains used in integration of the relaxation function.

These are in fact new, nonsymmetric, forms of the Staverman–Schwarzl formulae. To verify that these two forms are equal, one may interchange the order of integrations in the first form (30) and then switch the dummy variables ξ and η. Consequently, each of these two forms is equal to one half of their sum, and thus to (27). In the form on the first line, the second integral (over ξ) does not depend on θ anymore since θ is not greater than η. So this integral is a function of t and η only. Therefore, the first expression for $\mathscr{F}_\mu$ given by (30) may be substituted into (28). This provides the overall free energy density in the form:

$$\mathscr{F}(t)=\sum_{\mu=1}^{n}\int_{\theta=0^-}^{t}\int_{\eta=\theta}^{t}\left[\int_{\xi=\eta}^{t}\Psi_\mu(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta)\,\mathrm{d}v_\mu(\theta) \tag{32}$$

Now consider in this equation the integrals over θ and η, which cover the triangular domain shaded in Fig. 3c by means of vertical strips. However, the same domain can be covered by means of horizontal strips (Fig. 3d), which reveals that the triple integral in (29) is equal to the following:

$$\mathscr{F}(t)=\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}\sum_{\mu=1}^{n}\Psi_\mu(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\int_{\theta=0^-}^{\eta}\mathrm{d}v_\mu(\theta)\right]\mathrm{d}\varepsilon(\eta) \tag{33}$$

Thus the integration in θ may be performed separately, finally furnishing the expression:

$$\mathscr{F}(t)=\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}\sum_{\mu=1}^{n}v_\mu(\eta)\Psi_\mu(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{34}$$

In view of (22), this may be recognized to have the form (Fig. 3e):

$$\mathscr{F}(t)=\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}R(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{35}$$

But in (34) the order of integration may also be interchanged, giving

$$\mathscr{F}(t)=\int_{\xi=0}^{t}\left[\int_{\eta=0}^{\xi}\sum_{\mu=1}^{n}v_\mu(\eta)\Psi_\mu(2t-\xi-\eta)\,\mathrm{d}\varepsilon(\eta)\right]\mathrm{d}\varepsilon(\xi) \tag{36}$$

which may be recognized to have the form (Fig. 3f, g):

$$\mathscr{F}(t)=\int_{\xi=0}^{t}\left[\int_{\eta=0}^{\xi}R(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\eta)\right]\mathrm{d}\varepsilon(\xi)=\int_{\eta=0}^{t}\left[\int_{\xi=0}^{\eta}R(2t-\eta,\xi)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{37}$$

where in the last expression the dummy integration variables have been interchanged.

Thus we have obtained two equivalent expressions for $\mathscr{F}(t)$. Interchanging again the dummy variables and taking one half of their sum provides the following symmetric form:

$$\mathscr{F}(t)=\frac{1}{2}\int_{\eta=0}^{t}\left[\int_{\xi=0}^{\eta}R(2t-\eta,\xi)\,\mathrm{d}\varepsilon(\xi)+\int_{\xi=\eta}^{t}R(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{38}$$

We may also write $\mathscr{F}(t)$ in a symmetric form involving double integration over a square domain (Fig. 3h) with one single integrand like in the original Staverman–Schwarzl formula:

$$\mathscr{F}(t) = \frac{1}{2}\int_{\eta=0}^{t}\int_{\xi=0}^{t} \rho(t,\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{39}$$

in which

$$\rho(t,\xi,\eta) = \sum_{\mu=1}^{n} v_\mu[\min(\xi,\eta)]\Psi_\mu(2t-\xi-\eta) \tag{40}$$

This means that, for the upper and lower triangular parts of the square integration domain in Fig. 3h, i.e.,

$$\text{for } \xi \leqslant \eta\text{:}\quad \rho(t,\xi,\eta) = R(2t-\eta,\xi) \tag{41}$$

$$\text{for } \xi > \eta\text{:}\quad \rho(t,\xi,\eta) = R(2t-\xi,\eta) \tag{42}$$

or

$$\rho(t,\xi,\eta) = H(\xi-\eta)R(2t-\xi,\eta)+H(\eta-\xi)R(2t-\eta,\xi) \tag{43}$$

$$= R[2t-\max(\xi,\eta),\min(\xi,\eta)] = R[2t-\max(\xi,\eta),\xi+\eta-\max(\xi,\eta)] \tag{44}$$

where H denotes Heaviside step function. Because each $v_\mu(\xi)$ is a monotonically increasing function, $\Sigma_\mu v_\mu(\xi)\Psi_\mu(2t-\eta-\xi) < \Sigma_\mu v_\mu(\eta)\Psi_\mu(2t-\eta-\xi)$ if $\xi < \mu$. Consequently, function ρ may be more concisely defined as

$$\rho(t,\xi,\eta) = \min\,[R(2t-\eta,\xi), R(2t-\xi,\eta)] \tag{45}$$

The use of 'min' is a compact way to make the expressions for ρ symmetric with respect to ξ and η, i.e.

$$\rho(t,\xi,\eta) = \rho(t,\eta,\xi) \tag{46}$$

Function ρ may be called the symmetrized relaxation function. Combining (45) and (39), we acquire another compact expression:

$$\mathscr{F}(t) = \frac{1}{2}\int_{\eta=0}^{t}\int_{\xi=0}^{t} \min\,[R(2t-\eta,\xi), R(2t-\xi,\eta)]\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{47}$$

In contrast to the free energy expressions (35), (37) and (38), this expression as well as (39) has also the advantage that the integration limits do not depend on the integration variable (i.e., the integration domain is a square rather than two triangles).

Equation (47) provides the final result that we have been seeking—an expression for the Helmholtz free energy density in a solidifying viscoelastic material that does not involve the internal parameters v_μ and Ψ_μ. This equation generalizes the Staverman–Schwarzl formula from non-ageing to ageing linear viscoelastic materials. Same as the classical Staverman–Schwarzl formula, the new formula (47) is independent of the internal variables and gives the free energy density strictly in terms of the measurable (external) viscoelastic properties, namely the relaxation function and the macroscopic strain history.

7. Free energy as a potential for stress

Functional $\mathscr{F}$ is a sum of the free energies $\mathscr{F}_\mu \, \mathrm{d}v_\mu$ of non-ageing components $\mathrm{d}v_\mu$ (when these components exhibit instantaneous elasticity). These free energies are known to be potentials for the corresponding stresses $s_\mu(t)$. This raises the question whether, in the case of the solidification theory, $\mathscr{F}$ may represent a potential for the stress $\sigma(t)$. This means that the following property of a potential may be expected to apply:

$$\frac{\partial \mathscr{F}(t)}{\partial \varepsilon(t)} = \sigma(t) \tag{48}$$

We will now check whether it applies for the forms of the free energy we have derived.

In viscoelasticity without ageing, this property is known to be fulfilled for materials with instantaneous elasticity. In that case, the partial derivative is taken as the coefficient of the strain derivative at time t appearing in the time derivative of the functional $\mathscr{F}$, and is sometimes called the 'instantaneous partial derivative' of $\mathscr{F}$. Let us now consider ageing viscoelastic materials with free energy in the symmetrized form of (47). We now want to check whether indeed the property of a potential, expressed by (48), is also verified if we consider a viscoelastic material for which all the constituents exhibit instantaneous elasticity, that is, for which the relaxation function $R(t, t')$ is bounded from above, or the relaxation kernels Ψ_μ in (32) are bounded from above for all μ. Differentiating (47), we have

$$\begin{aligned}\frac{\partial \mathscr{F}(t)}{\partial \varepsilon(t)} = \frac{1}{2}\int_{\xi=0}^{t} \min\left[R(2t-\xi, t), R(2t-t, \xi)\right] \mathrm{d}\varepsilon(\xi) \\ + \frac{1}{2}\int_{\eta=0}^{t} \min\left[R(2t-t, \eta), R(2t-\eta, t)\right] \mathrm{d}\varepsilon(\eta)\, \mathrm{d}\varepsilon(\xi)\end{aligned} \tag{49}$$

Now, substituting $t = \xi + \Delta$ and taking into account the hardening condition in (26), we conclude that, in the first integral in (49), the second of the two relaxation functions is always the minimum, while in the second integral the first is always the minimum. So,

$$\frac{\partial \mathscr{F}(t)}{\partial \varepsilon(t)} = \frac{1}{2}\int_{\xi=0}^{t} R(t, \xi)\, \mathrm{d}\varepsilon(\xi) + \frac{1}{2}\int_{\eta=0}^{t} R(t, \eta)\, \mathrm{d}\varepsilon(\eta) \tag{50}$$

$$= \int_{t'=0}^{t} R(t, t')\, \mathrm{d}\varepsilon(t') = \sigma(t) \tag{51}$$

This proves that, if the material is solidifying and exhibits instantaneous elasticity, the free energy $\mathscr{F}(t)$ per unit volume of material is a potential for the stress.

Similarly, it may be proven that the free energy expressions in (35), (37), and (38) or (39), which do not depend on the hardening condition in (41), represent a potential. For example, differentiation of (35) provides

$$\frac{\partial \mathscr{F}(t)}{\partial \varepsilon(t)} = \int_{\xi=t}^{t} R(2t-\xi, t)\, \mathrm{d}\varepsilon(\xi) + \int_{\eta=0}^{t} R(2t-t, \eta)\, \mathrm{d}\varepsilon(\eta)$$

$$= \int_{\eta=0}^{t} R(t,\eta)\,\mathrm{d}\varepsilon(\eta) = \sigma(t) \tag{52}$$

8. Extension to more general ageing viscoelasticity

Equations (49), (51) and (52) indicate that if, conversely, the free energy is assumed at the outset to have one of the equivalent forms in (47), (35), (37), and (38) or (39), independently of the way we derived them, then the viscoelastic constitutive equation with ageing will be obtained from (52). As we will see later, this still ensures the Clausius–Duhem inequality to be satisfied provided an appropriate choice is also made for the expression of the dissipated power. By postulating such expressions for the free energy and the dissipation we define a class of linear ageing viscoelastic materials. Introducing such a definition, which is a converse of our initial approach, we realize that these expressions may be independent of the solidification theory (although our derivation from the solidification theory, which followed a deductive line of reasoning and was based on specific microscopic properties in addition the stress–strain relation, was necessary to actually obtain these expressions; they could have hardly been guessed intuitively).

In particular, the free energy density expressions in (47), (35), (37), and (38) or (39) do not depend on the condition of non-divergence (23) which characterizes the solidification theory, and they do not depend on any particular assumptions about the microscopic solidification process. Furthermore, these expressions for $\mathscr{F}$ except (47) do not depend on the hardening condition in (26). The only consequence of the hardening condition is to make possible the 'min' condition that makes the expression in (47) compact and symmetric.

Consider now the case of materials possessing no instantaneous elasticity. For a given constituent, this means that at least one unit in the Maxwell chain model consists only of a lonely dashpot (of viscosity $\eta_{0\mu}$), i.e., a dashpot (a dashpot with no spring coupled to it in series, or $E_{0\mu} \to \infty$). In that case, due to the uniform strain assumption adopted in the solidification theory, it suffices to add to the foregoing expression the viscous stress, provided that the corresponding singular Dirac kernel is not already included in the kernel R. This gives, for this more general case,

$$\sigma(t) = \frac{\partial \mathscr{F}(t)}{\partial \varepsilon(t)} + \eta\dot{\varepsilon} \quad \text{with } \eta = \sum_{\mu=1}^{n} v_{\mu}(t)\eta_{0\mu} \tag{53}$$

The theory of viscoelasticity developed by Mandel (1967a, b, 1974a, b, 1979) and Huet (1979, 1982, 1992) has thus been extended to the general and practically important class of ageing materials described by the solidification theory.

It may be noted that, except for the 'min' condition, the present expression for the free energy bears some similarity to the general form suggested in eqn (35) of Huet (1993a), provided that the kernel $R^*(t-u, t-v; t)$ in that equation as a function of three (rather than two) variables is put in the particular form $R(t+u, t-v)$. The corresponding expression of the free energy has again the property of a potential and the ensuing constitutive equation for stress corresponds to a special class of linear viscoelasticity with ageing. In this general context, the advantage of the solidification theory is that it provides a realistic and practically useful form and a physical basis of a microscopic origin for that vague and somewhat arbitrary choice of the relaxation kernel.

9. Complementary (Gibbs) free energy of solidifying material

A similar procedure can be applied to the expression (14) giving the negative of the density of the free enthalpy (or Gibbs free energy) for a non-ageing material. This leads to a similar result because the symmetry properties of the non-ageing creep functions Φ_μ of the constituents are the same as those of the non-ageing relaxation functions Ψ_μ. Defining the overall complementary energy density $\mathscr{F}^*$ of the solidifying material in the classical way as the negative of the free enthalpy density, i.e.

$$\mathscr{F}^*(t) = \sigma(t)\varepsilon(t) - \mathscr{F}(t) \tag{54}$$

we find the following five equivalent expressions:

$$\mathscr{F}^*(t) = \int_{\eta=0}^{t} \left[\int_{\xi=\eta}^{t} J(2t-\xi, \eta)\, \mathrm{d}\sigma(\xi) \right] \mathrm{d}\sigma(\eta) \tag{55}$$

$$= \int_{\eta=0}^{t} \left[\int_{\xi=0}^{\eta} J(2t-\eta, \xi)\, \mathrm{d}\sigma(\xi) \right] \mathrm{d}\sigma(\eta) \tag{56}$$

$$= \frac{1}{2} \int_{\eta=0}^{t} \left[\int_{\xi=0}^{\eta} J(2t-\eta, \xi)\, \mathrm{d}\sigma(\xi) + \int_{\xi=\eta}^{t} J(2t-\xi, \eta)\, \mathrm{d}\sigma(\xi) \right] \mathrm{d}\sigma(\eta) \tag{57}$$

$$= \frac{1}{2} \int_{\xi=0}^{t} \int_{\eta=0}^{t} \{\max\,[J(2t-\xi, \eta), J(2t-\eta, \xi)]\}\, \mathrm{d}\sigma(\xi)\, \mathrm{d}\sigma(\eta) \tag{58}$$

The last expression with 'max' follows by setting $\delta = \eta - \xi$ and $\theta = 2t - \xi + \Delta$ and noting that ageing (solidifying, age-hardening) materials satisfy the following condition:

$$J(\eta+\Delta, \xi+\Delta) \leqslant J(\theta, \xi) \quad (\Delta > 0) \tag{59}$$

which is the counterpart of (26). However, the expressions in (55)–(57) do not depend on this hardening condition, nor on the solidification theory with its non-divergence condition.

The expression in (58) represents a potential for the strain because:

$$\frac{\partial \mathscr{F}^*(t)}{\partial \sigma(t)} = \varepsilon(t) \tag{60}$$

The proof is similar to that given before for the Helmholtz free energy density.

In contrast to (48), these expressions for $\mathscr{F}^*$ are not contingent upon the aforementioned restriction on the existence of instantaneous elasticity. This dichotomy arises from the non-duality principle, which was enunciated (without attention to ageing) by Mandel (1967a, b, 1974b, 1979) in a much more general context. The non-duality principle postulates that, while the total stress may depend upon the instantaneous strain rate (a viscous effect), the total strain cannot depend upon the instantaneous stress rate. Mandel based his postulate on the available experimental results.

Based on his postulate, Mandel showed that the property of a potential expressed by (60) applies to every material with memory, whatever its behavior might be, provided that its instantaneous deformation either is elastic or vanishes. A dependence of the strain on the stress rate would in fact involve a possible singularity in the compliance kernel, thus yielding an additional term in the compliance function. But for the Maxwell chain there is no such singular term, even if an isolated dashpot (with no spring attached to it in series) is coupled in parallel with the other units of the chain (i.e., if one constituent is a viscous fluid). In that case, the instantaneous deformation under finite stress is vanishing, which corresponds to the second condition of ensuring that Mandel's non-duality principle allows the complementary energy to have the property of a potential. Equation (60) shows that the class of linear viscoelastic behavior with ageing described by the solidification theory satisfies the thermodynamic consequence of this principle.

10. Free energy in terms of compliance function

The free energy density can be obtained from the complementary energy by Legendre transformation inverse to (54),

$$\mathscr{F}(t) = \sigma(t)\varepsilon(t) - \mathscr{F}^*(t) \tag{61}$$

Substituting our previous results for σ and $\mathscr{F}^*$, one may derive for the representative volume element with ageing several equivalent expressions for the free energy density $\mathscr{F}$ in terms of the overall compliance function $J(t, t')$;

$$\begin{aligned}\mathscr{F}(t) &= \frac{1}{2}\int_{\eta=0}^{t}\left\{\int_{\xi=0}^{\eta}[2J(t,\xi)-J(2t-\eta,\xi)]\,\mathrm{d}\sigma(\xi)\right\}\mathrm{d}\sigma(\eta)\\ &\quad+\frac{1}{2}\int_{\eta=0}^{t}\left\{\int_{\xi=\eta}^{t}[2J(t,\xi)-J(2t-\xi,\eta)]\,\mathrm{d}\sigma(\xi)\right\}\mathrm{d}\sigma(\eta) \qquad (62)\\ &= \frac{1}{2}\int_{\xi=0}^{t}\int_{\eta=0}^{t}\{J(t,\xi)+J(t,\eta)-\max[J(2t-\xi,\eta),J(2t-\eta,\xi)]\}\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \qquad (63)\end{aligned}$$

This obviously reduces to the classical formula when there is no ageing. The symmetrizing 'max' condition is again contingent on the hardening condition (59), but the expression in (62) is independent of it and has more general validity than the initial solidification model.

11. Energy dissipation of solidifying material in terms of relaxation function

According to (8), the dissipation $\mathscr{D}$ is expressed in forms similar to the free energy except that the relaxation rate appears instead of the relaxation kernel. Therefore, the same procedure as before may be followed. In terms of the overall relaxation function, this gives the following four equivalent forms:

$$\mathscr{D}(t) = -2\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}\dot{R}(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{64}$$

$$\mathscr{D}(t) = -2\int_{\xi=0}^{t}\left[\int_{\eta=0}^{\xi}\dot{R}(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\eta)\right]\mathrm{d}\varepsilon(\xi) \tag{65}$$

$$\mathscr{D}(t) = -\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}\dot{R}(2t-\xi,\eta)\,\mathrm{d}\varepsilon(\xi)+\int_{\xi=0}^{\eta}\dot{R}(2t-\eta,\xi)\,\mathrm{d}\varepsilon(\xi)\right]\mathrm{d}\varepsilon(\eta) \tag{66}$$

$$\mathscr{D}(t) = -\int_{\eta=0}^{t}\int_{\xi=0}^{t}\dot{\rho}(t,\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{67}$$

Here $\dot{R}(t,t') = \partial R(t,t')/\partial t$, and the correct term in the 'min'-conditions has been picked by heeding the condition (26), which gives

$$\text{for } \xi \leqslant \eta\text{:}\quad \dot{\rho}(t,\xi,\eta) = \dot{R}(2t-\eta,\xi) \tag{68}$$

$$\text{for } \xi > \eta\text{:}\quad \dot{\rho}(t,\xi,\eta) = \dot{R}(2t-\xi,\eta). \tag{69}$$

Both expressions for $\dot{R}(t,t')$ correspond to the same time lag, $2t-\xi-\eta$. Because $\dot{R}(t,t') = \Sigma_\mu v_\mu(t')\dot{\Psi}_\mu(t-t')$ and $\dot{R}(t+\Delta,t'+\Delta) = \Sigma_\mu v_\mu(t'+\Delta)\dot{\Psi}_\mu(t-t') \leqslant \dot{R}(t,t')$ for $\Delta \geqslant 0$, and because functions $v_\mu(t)$ are increasing and $\dot{\Psi}_\mu < 0$, we conclude that the correct value of $\dot{\rho}$ corresponds to the maximum of the two $\dot{R}(t,t')$ values. From this, or directly from (26), it follows that $\mathscr{D}$ may also be written as

$$\mathscr{D} = -\int_{\eta=0}^{t}\int_{\xi=0}^{t}\max\left[\dot{R}(2t-\eta,\xi),\dot{R}(2t-\xi,\eta)\right]\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \tag{70}$$

The foregoing expressions can also be derived directly from the expression (47) for the free energy density using the general expression for the isothermal dissipated power in terms of the total power and the (isothermal) rate of change of the free energy density. This furnishes

$$\begin{aligned}\mathscr{D}(t) &= \sigma(t)\dot{\varepsilon}(t)-\dot{\mathscr{F}}(t) = \sigma(t)\dot{\varepsilon}(t)-\frac{1}{2}\dot{\varepsilon}(t)\int_{0}^{t}\min\left[R(2t-\xi,t),R(2t-t,\xi)\right]\mathrm{d}\varepsilon(\xi)\\ &\quad -\frac{1}{2}\dot{\varepsilon}(t)\int_{0}^{t}\min\left[R(2t-t,\eta),R(2t-\eta,t)\right]\mathrm{d}\varepsilon(\eta)-\int_{\eta=0}^{t}\int_{\xi=0}^{t}\dot{\rho}(t,\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \qquad (71)\\ &= \sigma(t)\dot{\varepsilon}(t)-\dot{\varepsilon}(t)\int_{0}^{t}R(t,t')\,\mathrm{d}\varepsilon(t')-\int_{\eta=0}^{t}\int_{\xi=0}^{t}\dot{\rho}(t,\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) \qquad (72)\\ &= -\int_{\eta=0}^{t}\int_{\xi=0}^{t}\dot{\rho}(t,\xi,\eta)\,\mathrm{d}\varepsilon(\xi)\,\mathrm{d}\varepsilon(\eta) > 0 \qquad (73)\end{aligned}$$

which coincides with (67).

In view of (22), the dissipation inequality is automatically satisfied because $\dot{R}(t,t') = \partial R(t,t')/\partial t < 0$ if the material is solidifying, i.e. age-hardening (or if it is non-ageing). Conversely, if one departs from the condition of positiveness of dissipation, it follows that $\dot{R}(t,t') < 0$, and thus R is proven to be a monotonically decreasing function of t. So, the expressions we obtained for the free energy and the dissipation conform to the Clausius–Duhem inequality in a local form.

Conversely, if the free energy is chosen a priori in the form of one of the equivalent expressions (47), (35), (37), and (38) or (39) without reference to any microstructural model, taking the dissipation in one of the foregoing equivalent forms is a necessary and sufficient condition to obtain a thermodynamically consistent model.

12. Energy dissipation of solidifying material in terms of compliance function

According to (15), the dissipation $\mathscr{D}$ may be expressed in forms similar to the free enthalpy density, except that the compliance rate appears instead of the compliance kernel. Therefore, the same procedure as before may be applied. In terms of the macroscopic compliance function J, this leads to the following four equivalent forms:

$$\mathscr{D}(t) = 2\int_{\eta=0}^{t}\left[\int_{\xi=\eta}^{t}\dot{J}(2t-\xi,\eta)\,\mathrm{d}\sigma(\xi)\right]\mathrm{d}\sigma(\eta) \tag{74}$$

$$= 2\int_{\eta=0}^{t}\left[\int_{\xi=0}^{\eta}\dot{J}(2t-\eta,\xi)\,\mathrm{d}\sigma(\xi)\right]\mathrm{d}\sigma(\eta) \tag{75}$$

$$= \int_{\eta=0}^{t}\left[\int_{\xi=0}^{\eta}\dot{J}(2t-\eta,\xi)\,\mathrm{d}\sigma(\xi)+\int_{\xi=\eta}^{t}\dot{J}(2t-\xi,\eta)\,\mathrm{d}\sigma(\xi)\right]\mathrm{d}\sigma(\eta) \tag{76}$$

$$= \int_{\xi=0}^{t}\int_{\eta=0}^{t}\{\max[\dot{J}(2t-\xi,\eta),\dot{J}(2t-\eta,\xi)]\}\,\mathrm{d}\sigma(\xi)\,\mathrm{d}\sigma(\eta) \tag{77}$$

where $\dot{J}(t,t') = \partial J(t,t')/\partial t$. The last expression with 'max' follows by setting $\delta = \eta-\xi$, $\tau = 2t-\xi$ and noting that ageing (solidifying, age-hardening) materials satisfy for positive δ the inequality

$$\dot{J}(\tau,\xi+\delta) \leqslant \dot{J}(\tau-\delta,\xi) \tag{78}$$

With this, all the basic thermodynamic functions of ageing viscoelasticity have been expressed without using internal variables. Thus, all of the Staverman–Schwarzl theory extended by Mandel has now been generalized to the case of ageing.

13. Generalization to isotropic materials under triaxial stress

Although, for the sake of brevity, our formulation has been restricted to uniaxial stress, a generalization to triaxial stress and strain is possible with a more general version of the theory obtained upon choosing the free energy a priori in the form of one of the equivalent expressions (47), (35), (37), and (38) or (39) and making use of the aforementioned properties of a potential. This is true even for anisotropic materials, in which case the ordinary products need to be replaced by appropriately contracted tensor products. The special case of isotropy will now be explained in some detail.

For isotropic materials, the viscoelastic behavior may be decoupled into volumetric and deviatoric parts, characterized by the volumetric and deviatoric relaxation functions $R_V(t, t')$ and $R_D(t, t')$. The total Helmholtz free energy density may be written as a sum of volumetric and deviatoric parts; $\mathscr{F} = \mathscr{F}_V + \mathscr{F}_D$. To make a symmetric expression possible, we may first suppose both $R_V(t, t')$ and $R_D(t, t')$ to satisfy the hardening conditions (26). Then if one assumes the volumetric and deviatoric components of the free energy to be in the form of (47), which have the property of a potential for stress and have kernels bounded from above (i.e., exhibiting no instantaneous inelastic strain), one obtains, by a similar procedure as before,

$$\mathscr{F}_V(t) = \frac{3}{2}\int_{\eta=0}^{t}\int_{\xi=0}^{t} \min\left[R_V(2t-\eta, \xi), R_V(2t-\xi, \eta)\right] \mathrm{d}\varepsilon^V(\xi)\, \mathrm{d}\varepsilon^V(\eta) \tag{79}$$

$$\mathscr{F}_D(t) = \frac{1}{2}\int_{\eta=0}^{t}\int_{\xi=0}^{t} \min\left[R_D(2t-\eta, \xi), R_D(2t-\xi, \eta)\right] \mathrm{d}\varepsilon_{ij}^D(\xi)\, \mathrm{d}\varepsilon_{ij}^D(\eta) \tag{80}$$

where subscripts i, j refer to components in Cartesian axes x_i, $i = 1, 2, 3$; $\varepsilon^V = \varepsilon_{kk}/3$ = volumetric strain, and $\varepsilon_{ij}^D = \varepsilon_{ij} - \delta_{ij}\varepsilon^V$ = deviatoric strain.

Generalizing any one of the equivalent expressions (35), (37), and (38) or (39), one obtains alternative expressions that do not require the hardening condition to be met;

$$\mathscr{F}_V(t) = 3\int_{\eta=0}^{t}\int_{\xi=0}^{\eta} R_V(2t-\eta, \xi)\, \mathrm{d}\varepsilon^V(\xi)\, \mathrm{d}\varepsilon^V(\eta) \tag{81}$$

$$= 3\int_{\eta=0}^{t}\int_{\xi=\eta}^{t} R_V(2t-\xi, \eta)\, \mathrm{d}\varepsilon^V(\xi)\, \mathrm{d}\varepsilon^V(\eta) \tag{82}$$

and

$$\mathscr{F}_D(t) = \int_{\eta=0}^{t}\int_{\xi=0}^{\eta} R_D(2t-\eta, \xi)\, \mathrm{d}\varepsilon_{ij}^D(\xi)\, \mathrm{d}\varepsilon_{ij}^D(\eta) \tag{83}$$

$$= \int_{\eta=0}^{t}\int_{\xi=\eta}^{t} R_D(2t-\xi, \eta)\, \mathrm{d}\varepsilon_{ij}^D(\xi)\, \mathrm{d}\varepsilon_{ij}^D(\eta) \tag{84}$$

Then, in view of the property of free energy as a potential, the constitutive equation may be written in the classical form used for the isotropic linear viscoelastic materials with ageing:

$$\sigma_{ij}(t) = 3\delta_{ij}\int_{\xi=0}^{t} R_V(t, \xi)\, \mathrm{d}\varepsilon^V(\xi) + \int_{\xi=0}^{t} R_D(t, \xi)\, \mathrm{d}\varepsilon_{ij}^D(\xi)$$

Furthermore, according to the Clausius–Duhem inequality, the dissipation may be expressed as $\mathscr{D} = \mathscr{D}_{\mathrm{V}} + \mathscr{D}_{\mathrm{D}}$ in which $\mathscr{D}_{\mathrm{V}}$ and $\mathscr{D}_{\mathrm{D}}$ are given by one of the following equivalent forms,

$$\mathscr{D}_{\mathrm{V}}(t) = 6\int_{\eta=0}^{t}\int_{\xi=0}^{\eta} \dot{R}_{\mathrm{V}}(2t-\eta,\xi)\,\mathrm{d}\varepsilon^{\mathrm{V}}(\xi)\,\mathrm{d}\varepsilon^{\mathrm{V}}(\eta) \tag{85}$$

$$= 6\int_{\eta=0}^{t}\int_{\xi=\eta}^{t} \dot{R}_{\mathrm{V}}(2t-\xi,\eta)\,\mathrm{d}\varepsilon^{\mathrm{V}}(\xi)\,\mathrm{d}\varepsilon^{\mathrm{V}}(\eta) \tag{86}$$

and

$$\mathscr{D}_{\mathrm{D}}(t) = 2\int_{\eta=0}^{t}\int_{\xi=0}^{\eta} \dot{R}_{\mathrm{D}}(2t-\eta,\xi)\,\mathrm{d}\varepsilon_{ij}^{\mathrm{D}}(\xi)\,\mathrm{d}\varepsilon_{ij}^{\mathrm{D}}(\eta) \tag{87}$$

$$= 2\int_{\eta=0}^{t}\int_{\xi=\eta}^{t} \dot{R}_{\mathrm{D}}(2t-\xi,\eta)\,\mathrm{d}\varepsilon_{ij}^{\mathrm{D}}(\xi)\,\mathrm{d}\varepsilon_{ij}^{\mathrm{D}}(\eta) \tag{88}$$

respectively. From this, the other thermodynamic functions can be obtained in similar generalized forms.

14. Thermodynamic functions in terms of Maxwell or Kelvin chain

Although the purpose of this paper has been to formulate the thermodynamic functions without using the material properties associated with the internal variables, expressions in terms of such properties are sometimes useful for computational algorithms. In the case of Maxwell chain with age-dependent moduli $E_\mu(t)$ and viscosities $\eta_\mu(t)$, such expressions may simply be obtained by substituting, into any of the foregoing expressions,

$$R(t,\xi) = \sum_{\mu=1}^{n} v_\mu(\xi)\Psi_\mu(t-\xi), \quad \Psi_\mu(t-\xi) = E_\mu^0\,\mathrm{e}^{-\frac{t-\xi}{\tau_\mu}} \tag{89}$$

where E_μ^0 are the moduli of the nonageing constituents of growing volumes $v_\mu(t)$, associated with the individual Maxwell units of the chain. $E_\mu(t) = E_\mu^0 v_\mu(t)$ and $\eta_\mu(t) = \tau_\mu E_\mu(t) = \tau_\mu E_\mu^0 v_\mu(t)$ are the age-dependent moduli and viscosities of the ageing Maxwell chain model of the material; see Bažant (1975, 1982); RILEM (1988). Similar expressions are available in these papers for the compliance function $J(t,\xi)$ corresponding to an ageing Kelvin chain model.

15. Conclusions

(1) The solidification theory for ageing materials, which represents a physically realistic model for viscoelasticity of ageing concrete caused by chemical solidification on the pores wall, allows the Staverman–Schwarzl formulae for the densities of Helmholtz free energy and for the dissipated power of a linear viscoelastic material to be generalized for the case of ageing.

Mandel's extensions of these expressions to the free enthalpy and dissipation in dual forms based on the relaxation and compliance functions can also be generalized.

(2) The advantage of these new formulae is that they express the thermodynamic functions in terms of only the measurable physical variables (the measured strain history, and the stress history determined from measured load history) and measurable viscoelastic characteristics (the relaxation and compliance functions)—in other words, that they do not involve the internal variables such as the partial stresses of Maxwell chain model nor the characteristics of the solidification process (volume growth functions v_μ) and the relaxation functions of the constituents (Ψ_μ), used in previous expressions for the thermodynamic functions of such materials.

(3) It is found that, aside from several other equivalent expressions, these thermodynamic functions can always be expressed as the double integral over strain or stress history on a square domain of a quadratic expression depending only on a symmetrized form of the relaxation function, or the compliance function, or their rates. The symmetrization can be reduced to taking a minimum or maximum of two relaxation or compliance functions (or their rates) with interchanged time variables.

(4) For materials exhibiting instantaneous elasticity, the partial derivative of the Helmholtz free energy density per unit volume of material with respect to the strain history yields the stress history. Thus the basic property of the free energy as a potential for the stress is extended to viscoelasticity with ageing described by the solidification theory. In absence of instantaneous elasticity, it suffices to add the (instantaneous) purely viscous stress to the stress obtained from the potential. The free enthalpy density is further proven to be a potential for the total strain history, which holds true even if instantaneous elasticity is absent. The dichotomy in the instantaneous elasticity restrictions can be related to Mandel's non-duality principle whose thermodynamic consequence turns out to apply also to the case of ageing.

(5) The dissipated power can be expressed in several ways as a quadratic double integral of the relaxation function rate over the strain history. In one of these forms, the relaxation function in the kernel is symmetrized by the use of a minimum condition.

(6) The formulae derived are thermodynamically admissible, satisfying the Clausius–Duhem inequality in the local form. This is important because the literature on concrete involves several examples of ageing formulations proposed for concrete creep that have later been shown to violate the dissipation inequality required by the second law of thermodynamics [e.g. Bažant (1982), RILEM (1988)].

(7) Although the solidification model for concrete has been used as a physically instructive starting point, the thermodynamic functions derived appear to have a more general validity. For isotropic materials characterized by the volumetric and deviatoric relaxation functions, these functions are explicitly extended to three dimensions. The extension to the anisotropic case may be obtained in the same straightforward fashion.

(8) The relationship between the expressions obtained here and the previous more general expressions of Huet (1993a) has been established.

(9) Among numerous applications that can be foreseen, the thermodynamic functions derived should be useful for obtaining bounds on the response of ageing linearly viscoelastic structures (as done in Huet, 1995b, for the non-ageing case). They should further be useful for deriving approximate solutions and for formulating numerical solution algorithms.

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References

Bažant, Z.P., 1972a. Numerical determination of long-range stress history from strain history in concrete. Materials and Structures (RILEM) 5, 135–141.

Bažant, Z.P., 1972b. Thermodynamics of interacting continua with surfaces and creep analysis of concrete structures. Nuclear Engineering and Design 20, 477–505.

Bažant, Z.P., 1975. Theory of creep and shrinkage in concrete structures: a precis of recent developments. In: Nemat-Nasser, S. (Ed.), Mechanics Today (Am. Acad. Mech.), vol. 2. Pergamon Press, 1975, pp. 1–93.

Bažant, Z.P., 1977. Viscoelasticity of porous solidifying material—concrete. J. of the Engng Mech. Div., ASCE 103, 1049-1067; Disc. 1979, 725–728.

Bažant, Z.P., 1979. Thermodynamics of solidifying or melting viscoelastic material. J. of the Engng Mech. Div., Proc. ASCE 105, 933–952.

Bažant, Z.P., 1982. Mathematical models for creep and shrinkage of concrete, In: Bažant, Z.P., Wittmann, F.H. (Eds.), Creep and Shrinkage in Concrete Structures, Chap. 7. John Wiley and Sons, London, pp. 163–256.

Bažant, Z.P., Baweja, S., 1995, In collaboration with RILEM Committee TC 107-GCS, Creep and shrinkage prediction model for analysis and design of concrete structures—model B3 (RILEM Recommendation). Materials and Structures (RILEM, Paris) 28, 357–365; with Errata, vol. 29 (March 1996), p. 126.

Bažant, Z.P., Kim, S.-S., 1978. Can the creep curves for different loading ages diverge? Cement and Concrete Research 8, 601–612.

Bažant, Z.P., Prasannan, S., 1989a. Solidification theory for concrete creep: I. Formulation. ASCE Journal of Engineering Mechanics 115 (8) 1691–1703.

Bažant, Z.P., Prasannan, S., 1989b. Solidification theory for concrete creep: II. Verification and application. ASCE Journal of Engineering Mechanics 115 (8) 1704–1725.

Bažant, Z.P., Hauggaard, A.B., Baweja, S., Ulm, F.-J., 1997a. Microprestress-solidification theory for concrete creep. I. ageing and drying effects. Journal of Engineering Mechanics, ASCE 123 (11), 1188–1194.

Bažant, Z.P., Hauggaard, A.B., Baweja, S., 1997b. Microprestress-solidification theory for concrete creep. II. Algorithm and verification. Journal of Engineering Mechanics, ASCE 123 (11), 1195–1201.

Biot, M.A., 1954. Theory of stress–strain relations in anisotropic viscoelasticity and relaxation phenomena. J. Appl. Phys. 25 (11), 1385–1391.

Boltzmann, L., 1874. Zur theorie der elastischen Nachwirkungen. Sitzungsbericht, Kaiserlich. Akad. Wiss., Wien, Math. Naturwiss. Klasse. 70 (II), 275.

Brun, L., 1965. Sur deux expressions, analogues à la formule de Clapeyron, donnant l'énergie libre et la puissance dissipée pour un corps viscoélastique. Comptes Rendus Ac. Sc. Paris 261, 41–44.

Brun, L., 1967. Thermodynamique et viscoélasticité. Cahiers du Groupe Français de Rhéologie, SEDOCAR, Paris, 4, I, 191–202.

Brun, L., 1969. Méthodes énergétiques dans les systèmes évolutifs linéaires. Journal de Mécanique, Paris, 8, 125–166.

Carol, I., Bažant, A.P., 1993. Viscoelasticity with ageing caused by solidification of non-ageing constituent. Journal of Engineering Mechanics, ASCE, 119 (11), 2252–2269.

Christensen, R.M., 1969. Viscoelastic properties of heterogeneous media. J. Mech. Phys. Solids 17, 23–41.

Christensen, R.M., 1982. Theory of Viscoelasticity. Academic Press, New York, pp. 248–251.

Coleman, B.N., 1964. Thermodynamics of materials with memory. Arch. Rational Mech. Anal. 17, 1–46.

Coleman, B.N., Mizel, V.J., 1964. Existence of caloric equations of state in thermodynamics. J. Chemical Physics 40, 1116–1125.

Day, W.A., 1972. The Thermodynamics of Simple Materials with Fading Memory. Springer-Verlag, Berlin.

Fréchet, M., 1910. Sur les fonctionnelles continues. Ann. Sc., Paris 27, 3, 193–216.

Huet, C., 1970a. Sur l'évolution des contraintes et déformations dans les systèmes multicouches constitués de matériaux viscoélastiques présentant du vieillissement. Comptes Rendus Ac. Sc. Paris 270, 213–216.

Huet, C., 1970b. Le séchage des pâtes argileuses et la mécanique des milieux continus évolutifs. Bulletin du Groupe Français des Argiles 23, 39–57.

Huet, C., 1973. Application à la viscoélasticité non linéaire du calcul symbolique à plusieurs variables. Rheologica Acta 12, 279–288.

Huet, C., 1974. Opérateurs matriciels en viscoélasticité linéaire avec vieillissement et application aux structures viscoélastiques hétérogènes. In: Hult, J. (Ed.), Mechanics of Visco-Elastic Media and Bodies. Springer, Berlin, pp. 131–146.

Huet, C., 1979. Sur la notion d'état local en rhéologie. Science et Techniques de l'Armement, 4, 611–652.

Huet, C., 1980, Adaptation d'un algorithme de Bažant au calcul des multilames viscoélastiques vieillissants. Materials and Structures, Paris 13, 74, 91–98.

Huet, C., 1982. Topics in thermodynamics of rheological behavior. Rheologica Acta 21, 360–365.

Huet, C., 1985. Relations between creep and relaxation functions in nonlinear viscoelasticity with or without ageing. Journal of Rheology 29 (3), 245–257.

Huet, C., 1992. Minimum theorems for viscoelasticity, Eur. J. Mech. A/Solids, 11 (5) 653–684.

Huet, C., 1993a. Some basic tools and pending problems in the development of constitutive equations for the delayed behaviour of concrete. In: Bažant, Z.P., Carol, I. (Eds.), Creep and Shrinkage of Concrete. Spon, London, pp. 189–200.

Huet, C., 1993b. An integrated approach of concrete micromechanics. In: Huet, C. (Ed.), Micromechanics of Concrete and Cementitious Composites. Presses Polytechniques et Universitaires Romandes, Lausanne, pp. 117–146.

Huet, C., 1995a. A continuum thermodynamics approach for studying microstructural effects on the non-linear fracture behaviour of concrete seen as a multicracked granular composite material. In: Wittmann, F.H. (Ed.), Fracture Mechanics of Concrete and Concrete Structures, vol. 2. Aedificatio, Freiburg, pp. 1089–1108.

Huet, C., 1995b. Bounds for the overall properties of viscoelastic heterogeneous and composite materials. Archives of Mechanics, Warsaw 47 (6) 1125–1155.

Huet, C., 1997. An integrated micromechanics and statistical continuum mechanics approach for studying the fracture behaviour of microcracked heterogeneous materials with delayed response. Engineering Fracture Mechanics, special issue on Statistical Fracture Mechanics, in press.

Kestin, J., 1974. Entropy and entropy production; discussion paper. Domingos, I.J.J.D. et al. (Eds.). Foundations of Continuum Thermodynamics. Macmillan, London, pp. 143–158.

Kestin, J., 1979. A Course in Thermodynamics. Hemisphere, New York; revised printing, 2 volumes.

Kestin, J., 1992. Local-equilibrium formalism applied to mechanics of solids. Int. J. Solids Structures (George Herrmann Anniversary Issue) 29 (14/15), 1827–1836.

Manel, J., 1957. Sur les corps viscoélastiques dont les propriétés dépendent de l'âge (On the viscoelastic bodies with age-dependent properties, in French). Comptes Rendus Ac. Sc. Paris 247, 175–178.

Mandel, J., 1964. Cours de Mécanique. Ecole Polytechnique, Paris.

Mandel, J., 1966. Cours de Mécanique des Milieux Continus. Gauthier-Villars. Paris, 2 volumes.

Mandel, J., 1967a. Application de la thermodynamique aux milieux viscoélastiques à élasticité nulle ou restreinte. Comptes Rendus Ac. Sc., Paris 264, 133–134.

Mandel, J., 1967b. Application de la thermodynamique aux milieux viscoélastiques. Archives of Mechanics, Warsaw 2.20, 181–188.

Mandel, J., 1974a. Un principe de correspondance pour les corps viscoélastiques linéaires vieillissants. In: Hult, J. (Ed.), Mechanics of Visco-Elastic Media and Bodies. Springer, Berlin, pp. 44–55.

Mandel, J., 1974b. Introduction à la Mécanique des Milieux Continus Déformables. Scientific Editions of Poland, Warsaw.

Mandel, J., 1979. Variables cachées, puissance dissipée, dissipativité normale. Sciences et Techniques de l'Armement, Paris, 53, 4, 525–538.

RILEM Committee TC 69 (1988). (Z. Bažant, Chairman), State of the art in mathematical modeling of creep and shrinkage of concrete. In Bažant, Z.P., Wiley, J. (Eds.), Mathematical Modeling of Creep and Shrinkage of Concrete. Chichester and New York, pp. 57–215.

Roscoe, R., 1950. Mechanical models for the representation of viscoelastic properties. Brit. J. Appl. Phys. 1, 171–173.

Staverman, A.J., Schwarzl, P., 1952a. Thermodynamics of viscoelastic behaviour (model theory). Proc. Acad. Sc., The Netherlands 55, 474–485.

Staverman, A.J., Schwarzl, P., 1952b. Non-equilibrium thermodynamics of visco-elastic behaviour. Proc. Acad. Sc., The Netherlands 55, 486–492.

Truesdell, C., 1969. Rational Thermodynamics. McGraw-Hill, New York.

Valanis, K.C., 1971. Irreversibility and existence of entropy. Int. J. Non-Linear Mechanics 6, 337–360.

Valanis, K.C., 1983. Partial integrability as a basis for the existence of entropy in irreversible systems. ZAMM 63, 73–80.

Volterra, V., 1887. Sopra le funzioni che dipendono da altre funzioni. R. C. Acad. Lincei 4 (3), 97–105.

Volterra, V., 1959. Theory of Functionals and of Integral and Integro-differential Equations (1925 Madrid Lectures). Dover, New York.