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A NEW VISCOELASTIC CONSTITUTIVE MODEL FOR CONTINUOUS MEDIA AT FINITE THERMOMECHANICAL CHANGES

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Abstract—This paper is concerned with the continuum formulation of a fully coupled thermomechanical constitutive model for highly deformable bodies with viscous dissipation. The three-dimensional material law is applicable to the thermomechanical characterization of elastomeric (high-polymeric) solids in the finite strain domain under varying temperature. The description is based on the concept of internal state variables and rational thermodynamics. The main goal of the presentation is to develop consistent constitutive equations for the *stress*, *entropy* and independent *internal variables* such that the second law of thermodynamics, in the form of the Clausius-Duhem inequality, is satisfied. Motivated by the significant difference in bulk and shear response of elastomers, the model employs a local decomposition of the deformation into a dilatational and an isochoric part. The framework of nonlinear thermoviscoelasticity presented herein is formulated entirely in the reference configuration and provides a sound continuum basis for approximation techniques such as the Finite-Element method. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION AND OVERVIEW

The continuum approach to a thermodynamic theory of a highly deformable thermoviscoelastic medium undergoing large thermomechanical changes relative to an equilibrium configuration is well established, see, e.g., the references by Truesdell and Toupin (1960), Green and Adkins (1960), Koh and Eringen (1963), Coleman and Noll (1963), Truesdell and Noll (1965), Chadwick and Seet (1971). As discussed in the review article by Hutter (1977) there are two basic approaches to the thermodynamics of a continuous medium: rational and irreversible thermodynamics. In the theory of rational thermodynamics the second law [in the Truesdell-Toupin form of the local Clausius-Duhem inequality, see Truesdell and Toupin (1960), eqn (258.3)] serves as a restriction on the constitutive equations for a continuous medium. Basically, the constitutive equations must be such that every thermodynamical process leads to positive entropy production. Dissipative models which satisfy this restriction—the so-called thermodynamically consistent constitutive equations—then satisfy balance laws and the second law of thermodynamics for any arbitrary process in the body. This theory is in contrast to irreversible thermodynamics where the second law serves as a restriction on the processes that can occur in the continuum body, see Hutter (1977). Within the rational thermodynamics framework models for materials with fading memory have been proposed by Coleman and Noll (1963), Coleman (1964a), (1964b), see also Truesdell and Noll (1965), section 96. An application to elastic continua under varying temperature using Coleman's unified thermodynamical theory (single-integral laws) was recently proposed by Gurtin and Hrusa (1991). However, models for fully coupled nonlinear thermoviscoelasticity which are applicable to numerous

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industrial engineering problems have not received much attention. This is the case studied herein.

The goal of this paper is to develop a new three-dimensional constitutive model, suitable for use within a Finite-Element(FE)-framework, which describes the thermoviscoelastic response of highly deformable continuous media, which is of special interest within the scope of rubber elasticity.

The development of the model is centered around the construction of a Helmholtz free energy function capable of accommodating anisotropic response and representing the coupled thermomechanical properties of polymeric materials in the finite-strain domain and in temperature ranges in which polymers exhibit stress relaxation. These characteristics are observed in elastomeric (high-polymeric) solids, which are composed of a cross-linked monolithic three-dimensional network—one example is vulcanized rubber in a temperature range of 100–150°C, see, e.g., Tobolsky *et al.* (1944).

The present work is based on a continuum formulation of the macroscopic thermoviscoelastic behavior of rubber-like solids at finite strains and is phenomenological in spirit; network defects (see, e.g., Mullins and Thomas (1960), Scanlan (1960)) or crystallinity effects, which appear in a highly stretched rubber (with anisotropic material behavior) are outside the scope of this paper.

The current approach employs nonlinear kinematics together with explicit thermodynamical constitutive laws for dissipative materials based on rational thermodynamics and on the concept of internal state variables, which goes back to Coleman and Gurtin (1967). The additional internal variables, which are not measurable and observable in phenomenological experiments, specify the thermodynamic state and are necessary to describe an irreversible system, see, e.g., Schapery (1964) among others. For other approaches see, e.g., Green and Tobolsky (1946), Koh and Eringen (1963), Bernstein *et al.* (1964), Christensen (1980), Lubliner (1985), Simo (1987).

The theoretical study of this paper starts with an additive decomposition of the thermodynamic potential into purely thermoelastic and non-equilibrium parts. This approach is motivated by the concept in Simo (1987) which describes an isothermal finite-strain viscoelastic model incorporating a damage mechanism. Given the thermodynamic potential, constitutive relations for the stress, entropy and internal variables follow by the standard Coleman and Noll argument, see Coleman and Noll (1963). The restrictions imposed by the second law are then expressed by an inequality condition on the viscous dissipation of the internal variable model. The viscous response is characterized by a linear rate (constitutive) equation governing the time-dependent internal state of the material. The evolution equation employed is of first order and is motivated by the viscoelastic theory with linear kinematics, see Valanis (1972). The simple convolution representation of the rate equation is numerically easy to handle, well-suited for large-scale computation, ensures incremental objectivity and can be numerically integrated for the nonlinear regime using, e.g., a second-order accurate mid-point rule, see, e.g., Simo (1987) and Govindjee and Simo (1992). Furthermore, it is shown that the proposed structure of the thermodynamical constitutive model is consistent with the second law of thermodynamics, which is an essential contribution of this work.

In the next section the free energy function is decomposed within the scope of volumetric/deviatoric finite elasticity, which is motivated by experimental observations. The split is based on an exact multiplicative decomposition of the deformation in terms of dilatational components and volume-preserving parts, initially proposed by Flory (1961). This concept was systematically explored by Ogden (1984), Simo *et al.* (1985), Lubliner (1985) and recently successfully applied in computational mechanics for the Ogden-based multiparameter strain energy function by Simo (1987), Simo and Taylor (1991), Holzapfel and Simo (1994).

The proposed formulation of the constitutive law is general in that it is valid for all thermoviscoelastic materials in the large strain domain which can be characterized by a continuous scalar function. A simple example using a Saint-Venant-Kirchhoff-type material clearly shows a physical interpretation of the outlined nonlinear viscoelastic model as a nonlinear multidimensional generalization of the (classical) rheological model of Maxwell-type.

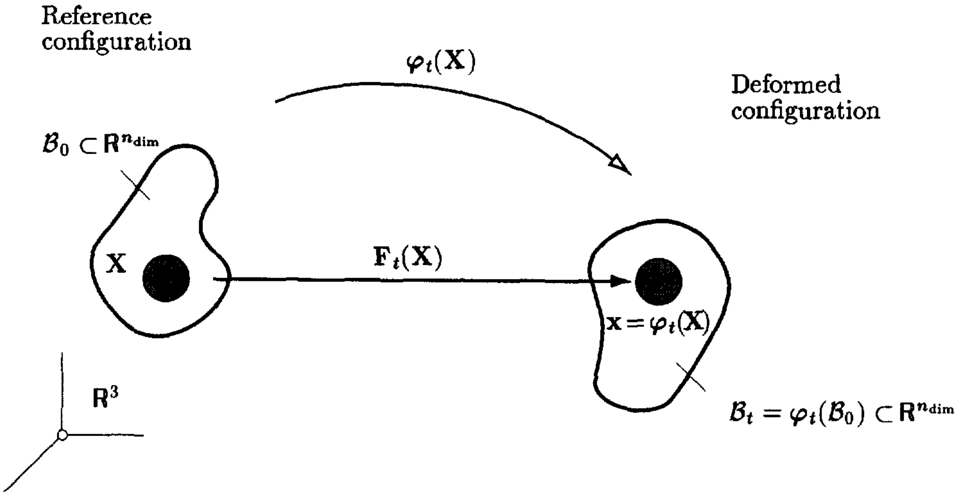

Fig. 1. Particle of a typical point in reference configuration and deformed configuration.

2. CONTINUUM FORMULATION

2.1. *Motion, constitutive assumptions*

Consider a continuum body composed of a thermoviscoelastic polymer material with reference placement $\mathscr{B}_0 \subset \mathbb{R}^{n_{\dim}}$ ($n_{\dim} = 1, 2$ or 3) and material particles $\mathbf{X} \in \mathscr{B}_0$, see Fig. 1. Denote by $\varphi_t(\mathbf{X}) : \mathscr{B}_0 \times \mathbb{R} \to \mathbb{R}^{n_{\dim}}$ a macroscopic motion of $\mathscr{B}_0$ in a time interval $t \in [0, T] \subset \mathbb{R}_+$ which maps any material point $\mathbf{X}$ to the point $\mathbf{x} = \varphi_t(\mathbf{X}) \in \mathbb{R}^3$ in the deformed configuration $\mathscr{B}_t = \varphi_t(\mathscr{B}_0) \subset \mathbb{R}^{n_{\dim}}$ and denote by $\Theta_t(\mathbf{X}) : \mathscr{B}_0 \times \mathbb{R} \to \mathbb{R}_+$ the absolute thermodynamic temperature field. Unless stated otherwise the reference configuration is assumed to be stress-free with homogeneous reference temperature $\Theta_0(>0)$.

As a measure of deformation we consider the material deformation gradient for the motion φ_t and the symmetric right Cauchy-Green strain tensor defined as

$$\left.\begin{aligned} \mathbf{F}_t(\mathbf{X}) &:= \frac{\partial \varphi_t(\mathbf{X})}{\partial \mathbf{X}} = \nabla \varphi_t \\ \mathbf{C}_t(\mathbf{X}) &:= \mathbf{F}_t^{\mathrm{T}}(\mathbf{X})\mathbf{F}_t(\mathbf{X}) \in \mathbb{M}_+^{n_{\dim}} \end{aligned}\right\} \quad \text{in } \mathscr{B}_0 \times [0, T], \tag{1}$$

where $\mathbb{M}_+^{n_{\dim}}$ is the set of $n_{\dim} \times n_{\dim}$ symmetric matrices characterized by $n_{\dim}$ real and positive eigenvalues $\lambda_{n_{\dim}}^2$—illustrated by the spectral decomposition $\mathbf{C}_t = \Sigma_{A=1}^3 \lambda_A^2 \mathbf{N}^{(A)} \otimes \mathbf{N}^{(A)}$ where $|\mathbf{N}^{(A)}| \equiv 1$, see, e.g., Ciarlet (1988), Simo and Taylor (1991). The symbolic operator $\nabla(\cdot)$ of tensor analysis is introduced for the gradient of $(\cdot)$ in the reference configuration and will be used throughout our developments.

The constitutive response of the thermoelastic continuum body is assumed to be fully elastic for infinitely slow deformation processes which is defined by a Helmholtz free energy function (per unit reference volume) $\Psi^\infty = \Psi^\infty(\mathbf{C}_t, \Theta_t) : \mathbb{M}_+^{n_{\dim}} \times \mathbb{R}_+ \to \mathbb{R}$.

To characterize the thermoviscoelastic response of the polymer we introduce a configurational free energy $\Upsilon = \Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^\alpha)$, where $\{\mathbf{\Gamma}_t^\alpha\}$ ($\alpha = 1, \ldots, m$) are a set of internal state variables each regarded as a strain tensor akin to the right Cauchy-Green strain tensor. In addition, the relaxation of the polymer chains is assumed to be governed by $m > 1$ relaxation (retardation) processes with given relaxation (retardation) times $\tau_\alpha = \tau_\alpha(\Theta) \in (0, \infty)$ ($\alpha = 1, \ldots, m$), which are, in general, temperature dependent.

2.2. *Balance laws*

Independent of the constitutive equations describing a material, the motion and temperature fields (assumed smooth) of a continuum body must satisfy local balance laws of mass, momentum and energy.

The local forms of balance of mass and momentum, given in the Lagrangian description (see, e.g., Truesdell and Noll (1965)), reads

$$\left.\begin{aligned} \rho_t(\mathbf{x})J_t(\mathbf{X}) &= \rho_0(\mathbf{X}) \\ \rho_0\ddot{\boldsymbol{\varphi}}_t(\mathbf{X}) &= \mathrm{Div}(\mathbf{F}_t\mathbf{S}_t)(\boldsymbol{\varphi}_t,\Theta_t)+\mathbf{B}_0(\mathbf{X}) \end{aligned}\right\} \quad \text{in } \mathscr{B}_0\times[0,T], \tag{2}$$

with

$$J_t^2(\mathbf{X}) = \det\mathbf{C}_t(\mathbf{X}) = [\det\mathbf{F}_t(\mathbf{X})]^2 > 0, \tag{3}$$

where $\rho_0(\mathbf{X}):\mathscr{B}_0\rightarrow\mathbb{R}_+$ is the mass density in the reference configuration and $\rho_t(\mathbf{x})$ denotes the mass density in the deformed configuration. Furthermore, J_t is the Jacobian determinant in $\mathscr{B}_0$. In the momentum balance equation the operator Div $(\cdot)$ is with respect to the coordinates $\mathbf{X}$ in $\mathscr{B}_0$, $\mathbf{S}_t$ denotes the symmetric second Piola–Kirchhoff stress tensor and $\mathbf{B}_0$ denotes the prescribed body force (per unit volume) in the reference configuration. Here and throughout the remainder of our developments we use superimposed dots to denote ordinary time derivatives. Balance of angular momentum implies the symmetry condition: $\mathbf{S}_t=\mathbf{S}_t^{\mathrm{T}}$.

Balance of energy in entropy form (the local evolution of specific entropy η_t appears explicitly) with the assumed presence of thermal gradients reads in the referential description

$$\Theta_t\dot{\eta}_t(\boldsymbol{\varphi}_t,\Theta_t) = -\mathrm{Div}\,\mathbf{H}_t(\boldsymbol{\varphi}_t,\Theta_t)+\mathscr{D}_{\mathrm{int}}+\mathscr{R} \quad \text{in} \quad \mathscr{B}_0\times[0,T], \tag{4}$$

with $\mathscr{R}$ the given specific heat supply, $\mathbf{H}_t$ the nominal heat flux vector, and $\mathscr{D}_{\mathrm{int}}$ the internal dissipation (local entropy production), which is zero for (perfect) elastic materials, see Truesdell and Noll (1965), section 80 and p. 320. An alternative version of eqn (4), which characterizes one form of the principle of dissipation, is

$$\mathscr{D}_{\mathrm{int}} = \mathbf{F}_t\mathbf{S}_t:\nabla\dot{\boldsymbol{\varphi}}_t+\Theta_t\dot{\eta}_t-\dot{e}_t \geqslant 0, \tag{5}$$

where e is referred to as the internal energy function, see Truesdell and Noll (1965), section 79. Relation (5) is known as the Clausius-Planck inequality and is one form of the second law of thermodynamics.

To complete the initial boundary value problem of motion for a continuum body the above set of nonlinear partial differential equations are supplemented by suitable boundary and initial conditions for the velocity, the motion and the entropy. Also, when heat transfer is considered a constitutive law for the heat flux is needed, which completes the continuum description of the thermoelastic material with heat conduction and viscous dissipation. A suitable constitutive equation motivated by experimental observations is the Fourier-Duhamel law of heat conduction which is of the form

$$\mathbf{H}_t = -\boldsymbol{\kappa}_0\mathbf{C}_t^{-1}\nabla\Theta_t, \tag{6}$$

where $\boldsymbol{\kappa}_0$ is the (reference) thermal conductivity tensor, which is positive definite. The referential heat flux vector is consistent with the classical Fourier (dissipation) inequality which in the reference configuration takes the form $\mathbf{H}_t\nabla\Theta_t\leqslant 0$, and is a crucial restriction on eqn (4), see Truesdell and Noll (1965), p. 295. For a thermally isotropic material the conductivity tensor becomes $\boldsymbol{\kappa}_0 = k_0(\Theta_t)\mathbf{I}$, where $k_0>0$ is the positive coefficient of thermal conductivity and $\mathbf{I}$ is the identity tensor.

Note that for vulcanized elastomers k_0 is temperature-dependent; in particular, the coefficient decreases linearly with increasing temperature, see Sircar and Wells (1981). For a FE-simulation of the nonlinear heat-conduction equation which includes deformation and temperature dependence for the heat flux see, e.g., Holzapfel and Simo (1994).

3. MATHEMATICAL MODEL

We consider a thermoviscoelastic model defined by the Helmholtz-free energy function

$$\Psi = \Psi^{\infty}(\mathbf{C}_t, \Theta_t) + \Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^{\alpha}). \tag{7}$$

Given that the thermodynamic state is characterized by the independent variables $(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^{\alpha})$ constitutive laws for the Piola-Kirchhoff stress $\mathbf{S}_t$, the entropy η_t (per unit reference volume) and the internal stress $\mathbf{Q}_t^{\alpha}$ follow in a standard way, see, e.g., Truesdell and Noll (1965):

$$\left.\begin{aligned} \mathbf{S}_t &= 2\nabla_{\mathbf{C}}\Psi^{\infty}(\mathbf{C}_t, \Theta_t) + 2\nabla_{\mathbf{C}}\Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^{\alpha}) \\ \eta_t &= \eta^{\infty} - \frac{\partial\Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^{\alpha})}{\partial\Theta} \quad \text{with} \quad \eta^{\infty} := -\frac{\partial\Psi^{\infty}(\mathbf{C}_t, \Theta_t)}{\partial\Theta} \\ \mathbf{Q}_t^{\alpha} &= -\nabla_{\mathbf{\Gamma}^{\alpha}}\Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^{\alpha}) \end{aligned}\right\} \text{ in } \mathscr{B}_0 \times [0, T]. \tag{8}$$

The variables $\{\mathbf{Q}_t^{\alpha}\}$ $(\alpha = 1, \ldots, m)$ are interpreted as the non-equilibrium stresses in the system and correspond—in analogy to the linear solid—with the internal history variables $\mathbf{\Gamma}_t^{\alpha}$ via the constitutive relation $(8)_3$. The entropy at equilibrium is labeled as η^{∞}.

In general a viscous solid generates heat in an irreversible manner through dissipation. The viscous dissipation of the internal variable model which arises from the Clausius-Duhem inequality, see Coleman and Gurtin (1967), is expressed using eqn $(8)_3$ in the following abstract inequality:

$$\mathscr{D}_{\text{int}} = \sum_{\alpha=1}^{m} -\nabla_{\mathbf{\Gamma}^{\alpha}}\Upsilon : \dot{\mathbf{\Gamma}}_t^{\alpha} = \sum_{\alpha=1}^{m} \mathbf{Q}_t^{\alpha} : \dot{\mathbf{\Gamma}}_t^{\alpha} \overset{!}{\geqslant} 0, \tag{9}$$

where $\dot{\mathbf{\Gamma}}_t^{\alpha}$ $(\alpha = 1, \ldots, m)$ denote the set of internal strain rates.

The simplest (fairly classical) evolution equations for the internal non-equilibrium stresses, which are motivated by a linear viscous model (standard linear solid) with internal variables, are of the form (see Valanis (1972), section 6, for an isothermal process):

$$\left.\begin{aligned} \dot{\mathbf{Q}}_t^{\alpha} + \frac{\mathbf{Q}_t^{\alpha}}{\tau_{\alpha}} &= \frac{\mathrm{d}}{\mathrm{d}t}[2\nabla_{\mathbf{C}}\Psi^{\alpha}(\mathbf{C}_t, \Theta_t)] - \mathbf{Q}_{\mathrm{cpl}\,t}^{\alpha} \\ \mathbf{Q}_t^{\alpha}|_{t=0} &= \mathbf{Q}_0^{\alpha} \end{aligned}\right\} \text{ in } \mathscr{B}_0 \times (0, T], \tag{10}$$

where $\Psi^{\alpha} = \Psi^{\alpha}(\mathbf{C}_t, \Theta_t) : \mathbb{M}_{+}^{n_{\dim}} \times \mathbb{R}_{+} \to \mathbb{R}$ is the free energy function of the polymer material which corresponds to the relaxation process α with $\tau_{\alpha} > 0$. Assuming instantaneous response the initial internal stresses are given by: $\mathbf{Q}_0^{\alpha} = 2\nabla_{\mathbf{C}}\Psi^{\alpha}(\mathbf{C}_0, \Theta_0)$. The additional term on the right hand side $\mathbf{Q}_{\mathrm{cpl}\,t}^{\alpha}$ contains temperature dependent material parameters and vanishes for isothermal processes. This second order tensor has to be determined such that evolution eqns (10) are dissipative and compatible with constitutive relation $(8)_3$. A successful FE-implementation of this class of rate equations for the isothermal regime was presented by Simo (1987) and for a model including damage variables by Govindjee and Simo (1992). It has been shown that eqn (10) provides a good approximation of the physical behavior in the large strain regime, see Simo (1987).

The simple structure of (10) admits a solution in the following (classical) convolution form

$$\mathbf{Q}_t^{\alpha} = \exp[-t/\tau_{\alpha}]\mathbf{Q}_0^{\alpha} + \mathscr{H}_t^{\alpha}, \tag{11}$$

with

$$\mathscr{H}_t^\alpha := \int_{0^+}^{t} \exp\left[-(t-s)/\tau_\alpha\right]\left\{\frac{\mathrm{d}}{\mathrm{d}s}[2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_s,\Theta_s)]-\mathbf{Q}_{\mathrm{cpl}\,s}^\alpha\right\}\mathrm{d}s. \tag{12}$$

Now, the main objective is to show that under suitable assumptions the proposed viscoelastic model satisfies the thermodynamic restriction imposed by the second law of thermodynamics (Clausius-Duhem inequality). In particular, we have to determine a form for the internal configurational free energy Υ which implies non-negative dissipation. This is the essence of the following:

Proposition: Motivated by linear viscoelastic theory assume:

(i) The internal configurational free energy Υ is quadratic in the internal strains Γ^α ($\alpha = 1,\dots,m$) in the sense that

$$\nabla^2_{\boldsymbol{\Gamma}^\alpha\boldsymbol{\Gamma}^\beta}\Upsilon = 2\delta_{\alpha\beta}\mu_\alpha(\Theta)\mathbb{I} \quad \text{(no sum on } \alpha\text{)}, \tag{13}$$

where μ_α defines a non-negative temperature dependent parameter and $\mathbb{I}$, $\delta_{\alpha\beta}$ denote the fourth-order identity tensor and the Kronecker delta, respectively.

(ii) The term $\mathbf{Q}_{\mathrm{cpl}\,t}^\alpha$ in evolution eqn $(10)_1$ is of the form

$$\mathbf{Q}_{\mathrm{cpl}\,t}^\alpha = 2\mu_\alpha\boldsymbol{\Gamma}_t^\alpha. \tag{14}$$

(iii) The viscous dissipation function $\mathscr{D}_{\mathrm{int}} \geqslant 0$ is of the form

$$\mathscr{D}_{\mathrm{int}} = \sum_{\alpha=1}^{m}\frac{1}{\eta_\alpha^*}|\mathbf{Q}_t^\alpha|^2 \geqslant 0, \quad \eta_\alpha^* := 2\mu_\alpha\tau_\alpha > 0 \tag{15}$$

where η_α^* is a coefficient associated to the α-relaxation process and $|(\cdot)|^2 = (\cdot):(\cdot)$.

(iv) The internal stresses evolve according to the proposed rate eqns (10) with (14).

Then the internal configurational free energy Υ is of the explicit form:

$$\Upsilon = \Upsilon(\mathbf{C}_t,\Theta_t,\boldsymbol{\Gamma}_t^\alpha) = \sum_{\alpha=1}^{m}\left[\mu_\alpha|\boldsymbol{\Gamma}_t^\alpha|^2 - 2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t,\Theta_t):\boldsymbol{\Gamma}_t^\alpha + \Psi^\alpha(\mathbf{C}_t,\Theta_t)\right]. \tag{16}$$

Proof: Comparing relation $(9)_2$ with (15) we obtain a dissipative evolution equation for the internal strains:

$$\mathscr{D}_{\mathrm{int}} = \sum_{\alpha=1}^{m}\mathbf{Q}_t^\alpha:\dot{\boldsymbol{\Gamma}}_t^\alpha = \sum_{\alpha=1}^{m}\frac{1}{\eta_\alpha^*}|\mathbf{Q}_t^\alpha|^2 \geqslant 0 \tag{17}$$

$$\mathbf{Q}_t^\alpha:\left[\dot{\boldsymbol{\Gamma}}_t^\alpha - \frac{1}{\eta_\alpha^*}\mathbf{Q}_t^\alpha\right] = 0 \quad \Rightarrow \dot{\boldsymbol{\Gamma}}_t^\alpha = \frac{\mathbf{Q}_t^\alpha}{\eta_\alpha^*}. \tag{18}$$

Time differentiation of eqn $(8)_3$ yields:

$$\dot{\mathbf{Q}}_t^\alpha + \sum_{\beta=1}^{m}[\nabla^2_{\boldsymbol{\Gamma}^\alpha\boldsymbol{\Gamma}^\beta}\Upsilon]\dot{\boldsymbol{\Gamma}}_t^\beta = -[2\nabla^2_{\boldsymbol{\Gamma}^\alpha\mathbf{C}}\Upsilon]\frac{\dot{\mathbf{C}}_t}{2} - [\nabla^2_{\boldsymbol{\Gamma}^\alpha\Theta}\Upsilon]\dot{\Theta}_t. \tag{19}$$

To obtain expressions for the right hand side of (19) consider integrating relation (13) twice. This gives

$$\nabla_{\mathbf{\Gamma}^\alpha}\Upsilon = 2\mu_\alpha(\Theta)\mathbf{\Gamma}_t^\alpha + \mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t), \tag{20}$$

and

$$\Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^\alpha) = \sum_{\alpha=1}^{m} [\mu_\alpha|\mathbf{\Gamma}_t^\alpha|^2 + \mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t) : \mathbf{\Gamma}_t^\alpha] + \Upsilon^*(\mathbf{C}_t, \Theta_t), \tag{21}$$

where $\mathbf{\Theta}_\alpha$ and Υ^* are tensor and scalar-valued functions, respectively. Now, observe from (20) that

$$\nabla^2_{\mathbf{\Gamma}^\alpha\mathbf{C}}\Upsilon = \nabla_{\mathbf{C}}\mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t) \quad \text{and} \quad \nabla^2_{\mathbf{\Gamma}^\alpha\Theta}\Upsilon = 2\mu'_\alpha\mathbf{\Gamma}_t^\alpha + \nabla_\Theta\mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t), \tag{22}$$

where $\mu'_\alpha := \partial\mu_\alpha(\Theta)/\partial\Theta$. Substituting eqns (13), $(18)_2$ and (22) into (19) gives

$$\dot{\mathbf{Q}}_t^\alpha + 2\mu_\alpha\frac{\mathbf{Q}_t^\alpha}{\eta_\alpha^*} = -[2\nabla_{\mathbf{C}}\mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t)]\frac{\dot{\mathbf{C}}_t}{2} - 2\mu'_\alpha\mathbf{\Gamma}_t^\alpha\dot{\Theta}_t - \nabla_\Theta\mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t)\dot{\Theta}_t. \tag{23}$$

By comparing this relation with evolution eqn $(10)_1$, using (14) and $(15)_2$ we observe that the left hand sides are identical. Taking the right hand sides we obtain the following important condition after integration with respect to time:

$$\mathbf{\Theta}_\alpha(\mathbf{C}_t, \Theta_t) = -2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t). \tag{24}$$

Substituting eqn (24) back into eqn (21) and taking $\Upsilon^*(\mathbf{C}_t, \Theta_t) = \Sigma_{\alpha=1}^m\Psi^\alpha(\mathbf{C}_t, \Theta_t)$ gives the expression for Υ in eqn (16). ■

Now, with functional (16) and constitutive eqn $(18)_2$ the model becomes:

$$\Psi = \Psi^\infty(\mathbf{C}_t, \Theta_t) + \sum_{\alpha=1}^{m} [\mu_\alpha|\mathbf{\Gamma}_t^\alpha|^2 - 2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t) : \mathbf{\Gamma}_t^\alpha + \Psi^\alpha(\mathbf{C}_t, \Theta_t)], \tag{25}$$

$$\left.\begin{aligned}
\mathbf{S}_t &= 2\nabla_{\mathbf{C}}\Psi^\infty(\mathbf{C}_t, \Theta_t) \\
&\quad + \sum_{\alpha=1}^{m} [2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t) - 4\nabla^2_{\mathbf{CC}}\Psi^\alpha(\mathbf{C}_t, \Theta_t)\mathbf{\Gamma}_t^\alpha] \\
\eta_t &= \eta^\infty(\mathbf{C}_t, \Theta_t) \\
&\quad + \sum_{\alpha=1}^{m} [\eta^\alpha(\mathbf{C}_t, \Theta_t) - 2\nabla_{\mathbf{C}}\eta^\alpha(\mathbf{C}_t, \Theta_t) : \mathbf{\Gamma}_t^\alpha - \mu'_\alpha|\mathbf{\Gamma}_t^\alpha|^2] \\
&\text{with} \\
\eta^\alpha &:= -\frac{\partial\Psi^\alpha(\mathbf{C}_t, \Theta_t)}{\partial\Theta} \quad \text{and} \quad \mu'_\alpha := \frac{\partial\mu_\alpha(\Theta)}{\partial\Theta} \\
\mathbf{Q}_t^\alpha &= \exp[-t/\tau_\alpha]\mathbf{Q}_0^\alpha + \mathscr{H}_t^\alpha = \eta_t^*\dot{\mathbf{\Gamma}}_t^\alpha \\
&\text{with} \\
\mathscr{H}_t^\alpha &= \int_{0^+}^{t} \exp[-(t-s)/\tau_\alpha]\left\{\frac{\mathrm{d}}{\mathrm{d}s}[2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_s, \Theta_s)]\right. \\
&\qquad \left. - 2\mu'_\alpha(\Theta_s)\mathbf{\Gamma}_s^\alpha\frac{\mathrm{d}\Theta_s}{\mathrm{d}s}\right\}\mathrm{d}s \\
\mathbf{\Gamma}_t^\alpha &= \frac{1}{\mu_\alpha}\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t) - \frac{1}{2\mu_\alpha}\mathbf{Q}_t^\alpha
\end{aligned}\right\} \text{ in } \mathscr{B}_0 \times [0, T]. \tag{26}$$

Herein, η^α characterizes the entropy which is associated to the relaxation process α.
Remark 3.1 :

(i) *Equilibrium*. Regarding eqn $(8)_3$ the condition for thermodynamic equilibrium is $\mathbf{Q}_t^\alpha = -\nabla_{\mathbf{\Gamma}^\alpha}\Upsilon(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^\alpha)|_{t\to\infty} \overset{!}{\equiv} \underset{\sim}{0}$, which in view of eqn (25) implies

$$\nabla_{\mathbf{\Gamma}^\alpha}\Psi(\mathbf{C}_t, \Theta_t, \mathbf{\Gamma}_t^\alpha) \equiv \sum_{\alpha=1}^{m} [2\mu_\alpha \mathbf{\Gamma}_t^\alpha - 2\,\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t)]|_{t\to\infty} = \underset{\sim}{0} \tag{27}$$

$$\Rightarrow \mathbf{\Gamma}_\infty^\alpha = \frac{1}{2\mu_\alpha} 2\,\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C}_t, \Theta_t). \tag{28}$$

Note that with eqn $(18)_2$ we have $\dot{\mathbf{\Gamma}}_t^\alpha|_{t\to\infty} \overset{!}{\equiv} \underset{\sim}{0}$, which goes along with the theorem of the thermoelastic limit, see also Truesdell and Noll (1965) p. 371. In addition, regarding eqn $(9)_2$ or eqn $(17)_1$, the dissipation vanishes at equilibrium, i.e., $\mathscr{D}_{\text{int}} \equiv 0$. In this case the thermodynamic process is reversible and the continuum reacts fully thermoelastic.

(ii) Since the viscoelastic behavior of elastomers is characterized by a medium composed of identical polymer chains, it is assumed that

$$\Psi^\alpha(\mathbf{C}_t, \Theta_t) = \beta_\infty^\alpha \Psi^\infty(\mathbf{C}_t, \Theta_t), \quad (\alpha = 1, \ldots, m) \quad \forall(\mathbf{C}_t, \Theta_t) \in \mathbb{M}_+^{n_{\text{dim}}} \times \mathbb{R}_+, \tag{29}$$

where $\beta_\infty^\alpha \in (0, \infty)$ are given non-dimensional constitutive parameters associated with $\tau_\alpha > 0$, see Govindjee and Simo (1992). With assumption (29) the set of constitutive relations (26) require only the specification of the Helmholtz free energy function Ψ^∞ for the hyperelastic body, which can be a completely arbitrary polyconvex function of $\mathbf{C}$ and Θ—a crucial advantage of the proposed model.

(iii) Regarding eqns $(26)_1$ and $(26)_2$, we observe an additive decomposition of the stress tensor and the entropy into equilibrium and non-equilibrium parts, respectively, which results from the structure given in (7).

(iv) Furthermore, note that the final form of the derived internal configurational free energy (16) Υ involves a gradient of the functional Ψ^α. In view of a finite element implementation the system of fundamental nonlinear eqns (26) necessitates an exact linearization procedure for solving the problem within Newton's method. Consequently, the (consistent) linearized tangent operators involve third derivatives of Υ with respect to the right Cauchy-Green strain tensor $\mathbf{C}_t$.

(v) A suitable thermodynamic potential for large strain and large temperature changes and its FE-implementation is described by Holzapfel and Simo (1994). The potential presented therein is based on the concept of entropy elasticity which falls within the context of statistical network theory and is closely related to the classical strain energy function proposed by Ogden (1972).

(vi) Recall that within the theory of finite thermoelasticity in general we observe three different thermomechanical coupling effects (see, e.g., Holzapfel and Simo 1994), i.e., (vi.a) the influence of temperature on the stresses (thermal stresses), (vi.b) structural thermoelastic heating (Gough–Joule effect) and (vi.c) geometric coupling, see eqn (6) (influence of deformation on the heat conduction). In addition, the proposed viscoelastic constitutive model (25) incorporates (vi.d) *dissipation* and (vi.e) *structural viscoelastic heating* defined by

$$\mathscr{S}_{\text{vis}} := -\sum_{\alpha=1}^{m} \Theta_t[\partial^2\Psi/\partial\Theta_t\,\partial\mathbf{\Gamma}_t^\alpha] : \dot{\mathbf{\Gamma}}_t^\alpha. \qquad \blacksquare$$

4. DILATATIONAL-DEVIATORIC MULTIPLICATIVE SPLIT

4.1. *Continuum basis, constitutive equations*

Most amorphous cross-linked polymers have a significant different response in bulk and shear. For rubber-like materials the ratio bulk modulus/shear modulus is often typically of order $\approx 10^3$ (Cyr (1988)), or higher. Consequently, the deformation response is nearly incompressible. Furthermore, the real physical viscoelastic behavior of most of the polymeric materials occurs strongly in shear and weaker in dilatation, see, e.g., Malvern (1969), p. 313.

Motivated by these experimental observations it is most beneficial to split the deformation locally into a dilatational and isochoric part, as originally proposed by Flory (1961). In particular, the deformation gradient at a point $\mathbf{X} \in \mathscr{B}_0$ at time $t < T$ is expressed as a multiplicative composition of isochoric and dilatational factors, i.e.,

$$\mathbf{F}_t(\mathbf{X}) := [J_t^{1/3}(\mathbf{X})\mathbf{I}]\bar{\mathbf{F}}_t(\mathbf{X}) \quad \text{in} \quad \mathscr{B}_0 \times [0, T], \tag{30}$$

with

$$\det \bar{\mathbf{F}}_t(\mathbf{X}) \equiv 1, \tag{31}$$

where $\bar{\mathbf{F}}_t$ describes the isochoric part (distortional response) of the deformation gradient and the Jacobian determinant $J_t(\mathbf{X})$ represents the dilatational part (volumetric response).

In view of eqns $(1)_2$ and (30) the strain measure $\bar{\mathbf{C}}_t$ corresponding to local isochoric deformation is

$$\bar{\mathbf{C}}_t(\mathbf{X}) := \bar{\mathbf{F}}_t^{\mathrm{T}}(\mathbf{X})\bar{\mathbf{F}}_t(\mathbf{X}) = [J_t^{-2/3}(\mathbf{X})\mathbf{I}]\mathbf{C}_t(\mathbf{X}) \quad \text{in} \quad \mathscr{B}_0 \times [0, T]. \tag{32}$$

For future reference we note that the partial (Fréchet) derivatives of $\bar{\mathbf{C}}_t$ and J_t relative to $\mathbf{C}$ are of the following form (see also Truesdell and Noll (1965)):

$$\left.\begin{aligned} \partial_{\mathbf{C}}\bar{\mathbf{C}}_t(\mathbf{X}) &= J^{-2/3}(\mathbf{X})[\mathbb{I} - \tfrac{1}{3}\mathbf{C}_t(\mathbf{X}) \otimes \mathbf{C}_t^{-1}(\mathbf{X})] \\ 2\,\partial_{\mathbf{C}}\mathrm{J}_t(\mathbf{X}) &= J_t(\mathbf{X})\mathbf{C}_t^{-1}(\mathbf{X}) \end{aligned}\right\}. \tag{33}$$

For notational simplicity, the subscript $(\cdot)_t$ will be suppressed throughout the remainder of the paper. Now, let us consider a specific free energy function Ψ^∞ of the form, see, e.g., Holzapfel and Simo (1994):

$$\Psi^\infty(\mathbf{C}, \Theta) = U^\infty(J, \Theta) + \bar{\Psi}^\infty(\bar{\mathbf{C}}, \Theta) + T^\infty(\Theta) \quad \forall(\mathbf{C}, \Theta) \in \mathbb{M}_+^{n_{\mathrm{dim}}} \times \mathbb{R}_+, \tag{34}$$

where U^∞ represents a convex volumetric response function, $\bar{\Psi}^\infty$ characterizes a polyconvex response function describing shear deformations of the polymer (see, e.g., Ciarlet (1988), chapter 4, for terminology), and the additive potential T^∞ represents a purely thermal contribution.

A straightforward application of the chain rule, relations (33) and (34), and basic rules of tensor analysis yield the following expression for the second Piola-Kirchhoff stress tensor

$$\left.\begin{aligned} &\mathbf{S}^\infty = 2\nabla_{\mathbf{C}}\Psi^\infty(\mathbf{C}, \Theta) = Jp\mathbf{C}^{-1} + J^{-2/3}\,\mathrm{Dev}\,[2\nabla_{\bar{\mathbf{C}}}\bar{\Psi}^\infty(\bar{\mathbf{C}}, \Theta)] \\ &\text{with} \quad p := \frac{\partial U^\infty(J, \Theta)}{\partial J} \quad \text{and} \quad \mathrm{Dev}\,[\cdot] := (\cdot) - \tfrac{1}{3}\mathrm{tr}\,[(\cdot)\mathbf{C}]\mathbf{C}^{-1} \end{aligned}\right\}, \tag{35}$$

where p denotes the hydrostatic pressure, Dev[$\cdot$] denotes the deviatoric projection operator for a tensor in the convected description and tr[$\cdot$] denotes the trace of the tensor [$\cdot$].

Performing a push-forward operation using relation (30) we obtain an expression for the Kirchhoff stress tensor at equilibrium. Namely,

$$\left.\begin{aligned} \boldsymbol{\tau}^{\infty} &= \mathbf{F}[2\nabla_{\mathbf{C}}\Psi^{\infty}(\mathbf{C},\Theta)]\mathbf{F}^{\mathrm{T}} = Jp\mathbf{I}+\operatorname{dev}[\boldsymbol{\tau}^{\infty}] \\ \text{with}\quad \operatorname{dev}[\boldsymbol{\tau}^{\infty}] &:= \bar{\mathbf{F}}\{\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\infty}(\bar{\mathbf{C}},\Theta)]\}\bar{\mathbf{F}}^{\mathrm{T}} \end{aligned}\right\}, \tag{36}$$

where dev[·] is the deviator in the spatial description.

We shall assume a material which exhibits a viscoelastic behavior *only in shear*—consequently the volume change of the material may be considered fully thermoelastic (time independent). In addition, the purely thermal potential T^{∞} is also considered to be time-independent. Hence, the deviatoric internal variables $\{\tilde{\mathbf{Q}}^{\alpha}\}$ $(\alpha = 1,\ldots,m)$ are governed by the following dissipative evolution equations

$$\left.\begin{aligned} &\dot{\tilde{\mathbf{Q}}}^{\alpha}+\frac{\tilde{\mathbf{Q}}^{\alpha}}{\tilde{\tau}_{\alpha}} = \frac{\mathrm{d}}{\mathrm{d}t}\{J^{-2/3}\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\alpha}(\bar{\mathbf{C}},\Theta)]\}-2\tilde{\mu}_{\alpha}'(\Theta)\tilde{\Gamma}^{\alpha}\frac{\mathrm{d}\Theta}{\mathrm{d}t} \\ &\tilde{\mathbf{Q}}^{\alpha}|_{t=0} = \tilde{\mathbf{Q}}_{0}^{\alpha} \end{aligned}\right\} \quad \text{in } \mathscr{B}_0\times(0,T], \tag{37}$$

which constitutes an appropriate counterpart of eqns (10) with (14). The constants $\tilde{\tau}_{\alpha}\in(0,\infty)$ $(\alpha = 1,\ldots,m)$ define the characteristic relaxation times for the m relaxation processes associated with *shear response* of the polymer material and $\tilde{\mu}_{\alpha}$ denote temperature dependent parameters.

Here we note that while the preceding developments are specialized to deviatoric viscoelastic response, the concepts may be easily extended to design models which account for dilatational viscoelastic response.

According to previous considerations the non-equilibrium deviatoric stress $\tilde{\mathbf{Q}}^{\alpha}$ and the associated internal *deviatoric* history variable $\tilde{\Gamma}^{\alpha}$ (which depend on the temperature and the deformation history) are related by the flow equation

$$\tilde{\mathbf{Q}}^{\alpha} = \tilde{\eta}_{\alpha}^{*}\dot{\tilde{\Gamma}}^{\alpha}, \tag{38}$$

where the parameter $\tilde{\eta}_{\alpha}^{*}$ has the characteristics of a Newtonian shear viscosity.

Within the preceding framework we next derive the time-dependent second Piola-Kirchhoff stress response using $(8)_1$, the configurational free energy of eqn (16), and the preceding assumptions on the viscoelastic response. Noting that the deviatoric part of $\mathbf{S}^{\alpha} := 2\nabla_{\mathbf{C}}\Psi^{\alpha}(\mathbf{C},\Theta)$ is given as $2\nabla_{\mathbf{C}}\tilde{\Psi}^{\alpha}(\bar{\mathbf{C}},\Theta) = J^{-2/3}\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\alpha}(\bar{\mathbf{C}},\Theta)]$, we use $(35)_1$ to obtain

$$\left.\begin{aligned} &\mathbf{S} = \mathbf{S}^{\infty}+\sum_{\alpha=1}^{m}\{J^{-2/3}\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\alpha}]-\tilde{\mathbb{C}}_{\mathrm{Dev}}^{\alpha}\tilde{\Gamma}^{\alpha}\} \\ &\text{with}\quad \tilde{\mathbb{C}}_{\mathrm{Dev}}^{\alpha} := 2\nabla_{\mathbf{C}}\{J^{-2/3}\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\alpha}]\} \end{aligned}\right\}, \tag{39}$$

where $\tilde{\mathbb{C}}_{\mathrm{Dev}}^{\alpha}$ denotes the deviatoric part of the material tangent moduli related to the α-relaxation (retardation) process. Performing a push-forward operation using the multiplicative decomposition (30), and employing the definition for $\operatorname{dev}[\boldsymbol{\tau}^{\alpha}]$ associated with $(36)_2$, we obtain the time-dependent Kirchhoff stress as

$$\boldsymbol{\tau} = \boldsymbol{\tau}^{\infty}+\sum_{\alpha=1}^{m}\{\operatorname{dev}[\boldsymbol{\tau}^{\alpha}]-\mathbf{F}(2\nabla_{\mathbf{C}}\{J^{-2/3}\operatorname{Dev}[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^{\alpha}]\}\tilde{\Gamma}^{\alpha})\mathbf{F}^{\mathrm{T}}\}. \tag{40}$$

Regarding the set of constitutive eqns (8) and (26) the stress is supplemented by the entropy η and the constitutive law for the deviatoric internal stress $\tilde{\mathbf{Q}}^{\alpha}$, which is derived in an analogous manner:

$$\eta = \eta^{\infty} + \sum_{\alpha=1}^{m} [\tilde{\eta}^{\alpha} - 2\,\nabla_{\mathbf{C}}\tilde{\eta}^{\alpha} : \tilde{\mathbf{\Gamma}}^{\alpha} - \tilde{\mu}'_{\alpha}|\tilde{\mathbf{\Gamma}}^{\alpha}|^{2}] \quad \text{with } \tilde{\eta}^{\alpha} := -\frac{\partial\tilde{\Psi}^{\alpha}(\tilde{\mathbf{C}},\Theta)}{\partial\Theta}, \tag{41}$$

$$\tilde{\mathbf{Q}}^{\alpha} = \exp[-t/\tilde{\tau}_{\alpha}]\tilde{\mathbf{Q}}^{\alpha}_{0} + \tilde{\mathscr{H}}^{\alpha} = \tilde{\eta}^{*}_{\alpha}\dot{\tilde{\mathbf{\Gamma}}}^{\alpha}, \tag{42}$$

with

$$\tilde{\mathscr{H}}^{\alpha}_{t} = \int_{0^{+}}^{t} \exp[-(t-s)/\tilde{\tau}_{\alpha}]\left\{\frac{\mathrm{d}}{\mathrm{d}s}[J^{-2/3}\,\mathrm{Dev}\,[2\,\nabla_{\tilde{\mathbf{C}}}\tilde{\Psi}^{\alpha}(\tilde{\mathbf{C}}_{s},\Theta_{s})]] - 2\tilde{\mu}'_{\alpha}(\Theta_{s})\tilde{\mathbf{\Gamma}}^{\alpha}_{s}\frac{\mathrm{d}\Theta_{s}}{\mathrm{d}s}\right\}\mathrm{d}s \tag{43}$$

and

$$\tilde{\mathbf{\Gamma}}^{\alpha} = \frac{1}{\tilde{\mu}_{\alpha}}J^{-2/3}\,\mathrm{Dev}\,[\nabla_{\tilde{\mathbf{C}}}\tilde{\Psi}^{\alpha}(\tilde{\mathbf{C}},\Theta)] - \frac{1}{2\tilde{\mu}_{\alpha}}\tilde{\mathbf{Q}}^{\alpha}. \tag{44}$$

In addition, using the free energy function (34) together with the assumptions on the viscoelastic response, eqn (29) becomes

$$\Psi^{\alpha}(\mathbf{C},\Theta) \equiv \tilde{\Psi}^{\alpha}(\tilde{\mathbf{C}},\Theta) = \tilde{\beta}^{\alpha}_{\infty}\tilde{\Psi}^{\infty}(\tilde{\mathbf{C}},\Theta), \quad (\alpha = 1,\ldots,m) \quad \forall(\mathbf{C},\Theta)\in\mathbb{M}^{n_{\mathrm{dim}}}_{+}\times\mathbb{R}_{+}, \tag{45}$$

where the constants $\tilde{\beta}^{\alpha}_{\infty}\in(0,\infty)$ $(\alpha = 1,\ldots,m)$ define the free energy factors for the retarded history associated with *shear response*.

For convenience, Box 1 summarizes the preceding coupled viscoelastic model within the context of a dilatational/deviatoric split. The model accommodates large strain and general anisotropic response.

Remark 4.1:

(i) It is well established that the phenomenon of chemical stress relaxation of cross-linked vulcanized rubbers is temperature dependent (see, e.g., Tobolsky (1960), chapter 5). The stress-decay which is characterized by a discrete relaxation spectra with m temperature dependent relaxation times can be explained by chemical rupture of the three-dimensional network.

In the low temperature range of the rubbery state the network show (nearly) no stress relaxation, but data which are based on stress relaxation-experiments for vulcanized rubbers at constant deformation have indicated a rapid stress-decay in the temperature range 100–150°C, see Tobolsky *et al.* (1944). Furthermore, experiments have shown that stress relaxation is independent of both the deformed state of the network and the absence or presence of carbon black fillers in the rubbers, Tobolsky *et al.* (1944). An experimental investigation of the effects of temperature on the constitutive response for silicon rubber was presented by Lee *et al.* (1966).

The relationship between the relaxation time and the absolute temperature is commonly characterized in the form of an exponential function—by the Arrhenius equation

$$\tilde{\tau} = A\exp[E_{\mathrm{act}}/R\Theta], \tag{46}$$

where A, E_{act} and R denote a numerical constant characteristic of the reacting substances, the activation energy of the relaxation and the thermodynamic gas constant, respectively. The form of the functional dependence of $\tilde{\tau}$ on Θ predicts the physical observation that viscoelastic effects occur faster as Θ increases. Equation (46) is representative of most polymer relaxations (Lee *et al.* (1966), Tobolsky *et al.* (1944)).

To incorporate the Arrhenius eqn (46) into the proposed dissipative evolution eqns (37) we suggest the convenient concept of "modified" time in which the relaxation time is hold fixed; for more details see, e.g., Knauss and Emri (1981) with more references therein.

(ii) The flow eqn (38) is analogous to the classical Newton's law, where $\dot{\tilde{\boldsymbol{\Gamma}}}^{\alpha}$ is interpreted as the shear strain rate of a dashpot and the quantity $\tilde{\eta}_{\alpha}^{*} > 0 \in (0, \infty)$ is interpreted as the coefficient of Newtonian shear viscosity of the α-relaxation process. The viscosity is related to the relaxation time $\tilde{\tau}$ and the modulus $2\tilde{\mu}_{\alpha}$ from rubber elasticity theory via $2\tilde{\mu}_{\alpha} = \tilde{\eta}_{\alpha}^{*}/\tilde{\tau}_{\alpha}$ which is motivated by a standard linear viscoelastic solid (Maxwell-model).

The vast majority of polymer behavior exhibits the well-known Newtonian "shear-thinning" phenomenon (pseudo-plasticity) which means that with respect to Newtonian characteristics the shear flow is faster as $\tilde{\mathbf{Q}}$ increases, see, e.g., Barnes *et al.* (1989), chapter 2. A model for both Newtonian and non-Newtonian materials is the popular "power-law"-model (see, e.g., Rosen (1979) with further references therein): $\tilde{\mathbf{Q}} = K\, \dot{\tilde{\boldsymbol{\Gamma}}}^{n}$, where n and K are parameters called the power-law factor or the flow behavior index and the "consistency", respectively. This model is widely used for engineering applications because it can be fit to experimental results for various materials and reduces to a Newtonian fluid for $n = 1$ with K known as the viscosity. Shear-thinning occurs if $n < 1$—for typical parameters see Barnes *et al.* (1989), p. 22. For an overview of different types of rheological models the reader is referred to Rosen (1979), Schoff (1988), p. 455.

4.2. *A simple example, rheological interpretation*

The goal of this section is to present a physical motivation of the derived viscoelastic model. Consider the following free energy function:

$$\Psi^{\alpha}(\mathbf{C}, \Theta) = \tfrac{1}{2}\mathbf{E} : \mathbb{C}^{\alpha}(\Theta) : \mathbf{E}, \tag{47}$$

where the Green–Lagrangian strain tensor $\mathbf{E}$ is associated to the right Cauchy-Green strain tensor via the well-known relation: $2\mathbf{E} = \mathbf{C} - \mathbf{I}$. The superscript α refers to a relaxation (retardation) process. In (47) $\mathbb{C}^{\alpha}$ denotes the positive definite elasticity tensor, which has temperature-dependent components of the assumed form $\mathbb{C}^{\alpha}(\Theta) = 2\mu_{\alpha}(\Theta)\mathbb{I}$, where $\mu_{\alpha}(\Theta) > 0$ characterizes the temperature dependent shear (Lamé) modulus of the viscoelastic "element" α.

The model (47) is the generalization of the St. Venant–Kirchhoff strain energy function to the thermoelastic regime, see, e.g., Ciarlet (1988) p. 155 for the St. Venant-Kirchhoff material. This classical isotropic nonlinear model is often used for engineering structures. Note that the Jacobian determinant (3) does not appear explicitly in this model. For the purpose of this section which is to give a physical interpretation of the proposed framework of thermoviscoelasticity based on the specific constitutive law (47), only the shear moduli are attached with the elasticity tensor.

By using eqn (16) the configurational energy with model (47) is

$$\Upsilon = \Upsilon(\mathbf{C}, \Theta, \boldsymbol{\Gamma}^{\alpha}) = \sum_{\alpha=1}^{m} \mu_{\alpha}(\Theta)|\mathbf{E} - \boldsymbol{\Gamma}^{\alpha}|^{2}.$$

By a straightforward differentiation of Υ with respect to $\boldsymbol{\Gamma}^{\alpha}$, the non-equilibrium stresses follow from $(8)_3$ together with eqn $(18)_2$ as

$$\mathbf{Q}^{\alpha} = -\nabla_{\boldsymbol{\Gamma}^{\alpha}}\Upsilon(\mathbf{C}, \Theta, \boldsymbol{\Gamma}^{\alpha}) = 2\mu_{\alpha}(\Theta)(\mathbf{E} - \boldsymbol{\Gamma}^{\alpha}) := \eta_{\alpha}^{*}\dot{\boldsymbol{\Gamma}}^{\alpha}, \tag{48}$$

which, in view of $(9)_2$, generates a positive dissipation $\mathscr{D}_{\text{int}} = \Sigma_{\alpha=1}^{m}|\mathbf{Q}^{\alpha}|^{2}/\eta_{\alpha}^{*} \geqslant 0$. From (10) and (14) the evolution equations for the non-equilibrium stresses are

Box 1: Coupled model problem for polymers within finite-strain thermoviscoelasticity—formulation based on volumetric-isochoric decomposition.

(i) Helmholtz free energy function:

$$\Psi(\mathbf{C},\Theta,\bar{\boldsymbol{\Gamma}}^\alpha) = \Psi^\infty(\mathbf{C},\Theta)+\sum_{\alpha=1}^{m}[\tilde{\mu}_\alpha|\bar{\boldsymbol{\Gamma}}^\alpha|^2-2\nabla_{\mathbf{C}}\Psi^\alpha(\mathbf{C},\Theta):\bar{\boldsymbol{\Gamma}}^\alpha+\Psi^\alpha(\mathbf{C},\Theta)]$$

with

$$\Psi^\infty(\mathbf{C},\Theta) = \mathrm{U}^\infty(J,\Theta)+\tilde{\Psi}^\infty(\bar{\mathbf{C}},\Theta)+T^\infty(\Theta),\quad \Psi^\alpha(\mathbf{C},\Theta) = \tilde{\beta}^\alpha_\infty\tilde{\Psi}^\infty(\bar{\mathbf{C}},\Theta)$$

(ii) Second Piola-Kirchhoff stress $[\bar{\mathbf{F}} = J^{-1/3}\mathbf{F}\,;\bar{\mathbf{C}} := \bar{\mathbf{F}}^{\mathrm{T}}\bar{\mathbf{F}} = J^{-2/3}\mathbf{C}]$:

$$\mathbf{S} = \mathbf{S}^\infty+\sum_{\alpha=1}^{m}\tilde{\beta}^\alpha_\infty\{J^{-2/3}\,\mathrm{Dev}\,[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^\infty]-\tilde{\mathbb{C}}^\infty_{\mathrm{Dev}}\bar{\boldsymbol{\Gamma}}^\alpha\}$$

with

$$\mathbf{S}^\infty = 2\nabla_{\mathbf{C}}\Psi^\infty(\mathbf{C},\Theta),\quad \tilde{\mathbb{C}}^\infty_{\mathrm{Dev}} := 2\nabla_{\mathbf{C}}\{J^{-2/3}\,\mathrm{Dev}\,[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^\infty]\}$$

(iii) Entropy:

$$\eta = \eta^\infty+\sum_{\alpha=1}^{m}[\tilde{\beta}^\alpha_\infty(\tilde{\eta}^\infty-2\nabla_{\mathbf{C}}\tilde{\eta}^\infty:\bar{\boldsymbol{\Gamma}}^\alpha)-\tilde{\mu}'_\alpha|\bar{\boldsymbol{\Gamma}}^\alpha|^2]$$

with

$$\eta^\infty := -\frac{\partial\Psi^\infty(\mathbf{C},\Theta)}{\partial\Theta},\quad \tilde{\eta}^\infty := -\frac{\partial\tilde{\Psi}^\infty(\bar{\mathbf{C}},\Theta)}{\partial\Theta},\quad \tilde{\mu}'_\alpha := \frac{\partial\tilde{\mu}_\alpha(\Theta)}{\partial\Theta}$$

(iv) Dissipation:

$$\mathscr{D}_{\mathrm{int}} = \sum_{\alpha=1}^{m}\frac{1}{\tilde{\eta}^*_\alpha}|\tilde{\mathbf{Q}}^\alpha|^2 \geqslant 0$$

with

$$\tilde{\mathbf{Q}}^\alpha = \exp[-t/\tilde{\tau}_\alpha]\tilde{\mathbf{Q}}^\alpha_0+\tilde{\mathscr{H}}^\alpha = \tilde{\eta}^*_\alpha\dot{\bar{\boldsymbol{\Gamma}}}^\alpha$$

$$\tilde{\mathscr{H}}^\alpha = \int_{0^+}^{t}\exp[-(t-s)/\tilde{\tau}_\alpha]\left\{\frac{\mathrm{d}}{\mathrm{d}s}[J^{-2/3}\tilde{\beta}^\alpha_\infty\,\mathrm{Dev}\,[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^\infty_s]]-2\tilde{\mu}'_{\alpha s}\bar{\boldsymbol{\Gamma}}^\alpha_s\frac{\mathrm{d}\Theta_s}{\mathrm{d}s}\right\}\mathrm{d}s$$

and

$$\bar{\boldsymbol{\Gamma}}^\alpha = \frac{1}{\tilde{\mu}_\alpha}\tilde{\beta}^\alpha_\infty J^{-2/3}\,\mathrm{Dev}\,[\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^\infty]-\frac{1}{2\tilde{\mu}_\alpha}\tilde{\mathbf{Q}}^\alpha$$

(v) Evolution equation:

$$\dot{\tilde{\mathbf{Q}}}^\alpha+\frac{\tilde{\mathbf{Q}}^\alpha}{\tilde{\tau}_\alpha} = \tilde{\beta}^\alpha_\infty\frac{\mathrm{d}}{\mathrm{d}t}\{J^{-2/3}\,\mathrm{Dev}\,[2\nabla_{\bar{\mathbf{C}}}\tilde{\Psi}^\infty]\}-2\tilde{\mu}'_\alpha\bar{\boldsymbol{\Gamma}}^\alpha\frac{\mathrm{d}\Theta}{\mathrm{d}t}$$

$$\tilde{\mathbf{Q}}^\alpha|_{t=0} = \tilde{\mathbf{Q}}^\alpha_0$$

$$\left.\begin{aligned}\dot{\mathbf{Q}}^\alpha+\frac{\mathbf{Q}^\alpha}{\tau_\alpha} &= 2\mu_\alpha(\Theta)\dot{\mathbf{E}}+2\dot{\mu}_\alpha(\mathbf{E}-\boldsymbol{\Gamma}^\alpha)\\ \mathbf{Q}^\alpha|_{t=0} &= \mathbf{Q}^\alpha_0\end{aligned}\right\}\ \text{in } \mathscr{B}_0\times[0,T]. \tag{49}$$

The stress response at time t is obtained with eqn $(26)_1$ and definition $(35)_1$

$$\mathbf{S} = \mathbf{S}^\infty+\sum_{\alpha=1}^{m}\underbrace{2\mu_\alpha(\Theta)(\mathbf{E}-\boldsymbol{\Gamma}^\alpha)}_{\overset{!}{=}\mathbf{Q}^\alpha[\text{eqn }(48)_2]}, \tag{50}$$

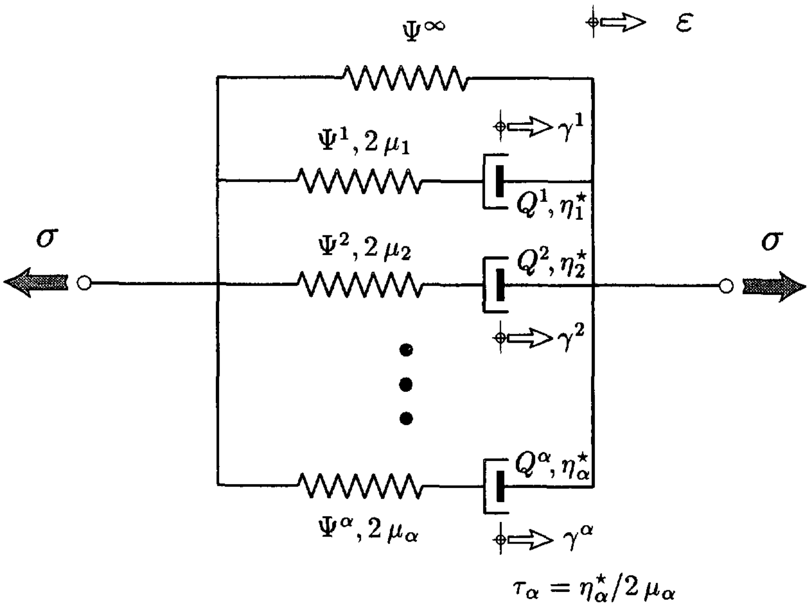

Fig. 2. Generalized Maxwell model—one-dimensional rheological interpretation.

which can be regarded as a *superposition* of the equilibrium and non-equilibrium stresses. Note that the internal variables $\mathbf{Q}^\alpha$ vanish at $t \to \infty$, as shown in Remark 3.1(i). Regarding the entropy generated by the relaxation process, we use eqn $(26)_2$ to obtain $\eta = \eta^\infty + \Sigma_{\alpha=1}^{m}[\eta^\alpha + 2\mu'_\alpha(\mathbf{E}:\mathbf{\Gamma}^\alpha - \frac{1}{2}|\mathbf{\Gamma}^\alpha|^2)]$, with $\eta^\alpha(\mathbf{C},\Theta) = -\mu'_\alpha|\mathbf{E}|^2$, which completes the thermodynamical description.

4.2.1. *Rheological interpretation.* A rheological representation of the proposed phenomenological thermoviscoelastic model can be understood as a generalization of a one-dimensional linear model, as illustrated in Fig. 2. The stored energy function associated with viscoelastic "element" α is assumed to be $\Psi^\alpha(\varepsilon,\Theta) = \frac{1}{2}[2\mu_\alpha(\Theta)\varepsilon^2]$ and $\Psi^\infty = \Psi^\infty(\varepsilon,\Theta)$, where the infinitesimal strains are denoted by ε and the spring-stiffnesses in the elements are labeled by μ_α.

The stresses in the dashpots Q^α follow merely by equilibrium from Fig. 2 and are governed by the constitutive law:

$$Q^\alpha = 2\mu_\alpha(\Theta)[\varepsilon - \gamma^\alpha] = \eta_\alpha^\star \dot{\gamma}^\alpha, \tag{51}$$

with coefficients $\eta_\alpha^\star > 0$ for the viscous elements and with the inelastic strain γ^α for the α-device. Time differentiation of $(51)_1$, use of $(51)_2$ and relation $2\mu_\alpha = \eta_\alpha^\star/\tau_\alpha$ yields the evolution equations for the internal variables

$$\dot{Q}^\alpha + \frac{Q^\alpha}{\tau_\alpha} = 2\mu_\alpha(\Theta)\dot{\varepsilon} + 2\dot{\mu}_\alpha(\varepsilon - \gamma^\alpha). \tag{52}$$

With respect to the thermoviscoelastic device of Fig. 2 the total stress σ is obtained by superposition of the equilibrium stress $\sigma^\infty := \partial\psi^\infty(\varepsilon,\Theta)/\partial\varepsilon$ and the non-equilibrium stresses Q^α in the dashpots by relation (balance of forces)

$$\sigma = \sigma^\infty + \sum_{\alpha=1}^{m} Q^\alpha. \tag{53}$$

For the thermostatic limit Q^α vanishes and the equilibrium stress σ^∞ associated with potential Ψ^∞ remains in the spring.

Note that the equilibrium equation and the classical constitutive relation for shear viscosity (51), the evolution eqns (52) and the total stress (53) remarkably constitutes the one-dimensional linear counterpart of eqns (48)–(50), respectively. In this sense, our proposed material model which is capable to describe relaxation (retardation) processes within the coupled thermomechanical regime can be viewed as a *nonlinear multi-dimensional generalization* of the linear thermomechanical device illustrated in Fig. 2.

5. SUMMARY AND CONCLUSIONS

A coupled thermomechanical nonlinear constitutive model for dissipative continuous media capable of accommodating stress-relaxation in large strain domains has been presented. The mathematical structure of the three-dimensional viscoelastic model is based on the concept of internal state variables and has a sound thermodynamical foundation. The free energy function is decomposed into a fully thermoelastic part and a configurational free energy, which governs the viscous response (only in shear) of the continuum. Furthermore, the model is written within the framework of volumetric/deviatoric finite thermoelasticity. A particular example furnished by a free energy function of a St. Venant–Kirchhoff-type material has shown a physical interpretation of the physically nonlinear thermoviscoelastic model. A rheological interpretation was given within the linear regime.

Our main concern was to develop a constitutive model that was compatible with the second law of thermodynamics and well-suited for numerical treatment within the Finite-Element-method. A numerical realization is the goal of future work.

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