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A thermo-mechanically coupled theory for large deformations of amorphous polymers. Part I: Formulation

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A thermo-mechanically-coupled theory for large deformations of amorphous polymers. Part I: formulation

Lallit Anand,* Nicoli M. Ames, Vikas Srivastava, and Shawn A. Chester
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

Abstract

In this Part I, of a two-part paper, we present a detailed continuum-mechanical development of a thermo-mechanically coupled elasto-viscoplasticity theory to model the strain rate and temperature dependent large-deformation response of amorphous polymeric materials. Such a theory, when further specialized (Part II) should be useful for modeling and simulation of the thermo-mechanical response of components and structures made from such materials, as well as for modeling a variety of polymer processing operations.

1 Introduction

Amorphous thermoplastic polymers are important engineering materials which are widely used in a variety of applications (cf., e.g., Haward and Young, 1997). Over the past twenty-five years considerable effort has been devoted to develop constitutive models to represent the large deformation elastic-viscoplastic behavior of these materials (e.g., Parks et al., 1985; Boyce et al., 1988; Arruda and Boyce, 1993, Wu and Van der Giessen, 1993; Govaert et al., 2000; Anand and Gurtin, 2003). Although differing in detail, these models combine three-dimensional representations of linear elasticity, of non-Newtonian viscoplastic flow arising from the motion of polymer segments, and of stiffening arising due to the alignment and locking of the long-chain polymer molecules at large strains, in a manner similar to that which was originally proposed in a one-dimensional setting by Haward and Thackray (1968). These models have been primarily used to describe the isothermal deformation of polymeric components below their glass transition temperatures. However, thermo-mechanical coupling effects have also been studied; for example, Arruda et al. (1995) have studied the effects of adiabatic heating under nominally homogeneous deformations, while Van der Giessen and co-workers (e.g., Basu and Van der Giessen, 2002; Estevez et al., 2005; Estevez and Basu, 2008) have studied the effects of adiabatic heating in the context of effects of temperature changes on the fracture response at cracks and notches under high-rate mode-I loading.

It is the purpose of this Part I, of a two-part paper, to present a detailed continuum-mechanical development of a *thermo-mechanically coupled*, large-deformation elasto-viscoplasticity theory to model the strain rate and temperature dependent large-deformation response of amorphous polymeric materials. Special forms of our theory also lead to a known class of constitutive models for viscoplasticity of elastomeric materials as proposed, for example, by Lion (1997), Reese and Govindjee (1998), Bergström and Boyce (1998, 2001), and Haupt and Sedlan (2001).

An essential kinematical ingredient of modern elasto-viscoplastic constitutive theories for amorphous polymers is the classical multiplicative decomposition (Kröner, 1960; Lee 1969)

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p \tag{1.1}$$

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*Corresponding author. Tel.: +1-617-253-1635; E-mail address: anand@mit.edu

of the deformation gradient $\mathbf{F}$ into elastic and plastic parts $\mathbf{F}^e$ and $\mathbf{F}^p$ (e.g., Boyce et al., 1988, Arruda and Boyce, 1993; Wu and Van der Giessen, 1993; Govaert et al., 2000; Anand and Gurtin, 2003). Following these authors we adopt this kinematical decomposition, and following Anand and Gurtin (2003) we develop the theory based on the *principle of virtual power*. However, the theory developed here differs from the isothermal theory of Anand and Gurtin (2003) in three major respects:

1. The theory is fully-thermomechanically coupled.

2. The rapid increase in stresses at large deformations as the polymer chains start to lock-up is modeled differently. Instead of having the free-energy depend on $\mathbf{F}^p$ through $\mathbf{B}^p = \mathbf{F}^p\mathbf{F}^{p\top}$, we follow the non-linear viscoelastic models of Lion (1997), Reese and Govindjee (1998) and Bergström and Boyce (1998, 2001) and take the free energy representing the underlying rubber-like non-linear elastic response to depend on the total deformation gradient $\mathbf{F}$ through $\mathbf{C} = \mathbf{F}^\top\mathbf{F}$.

3. Polymeric materials exhibit a pronounced *Bauschinger-like* effect upon unloading, even at moderate strain levels which are much smaller than those associated with the locking of polymeric chains at large strains (cf., e.g., Hasan and Boyce, 1995; Anand and Ames, 2006).[1] In order to allow for important *energy storage mechanisms* due to plastic deformation, the development of an *internal back-stress*, and to account for Bauschinger-like phenomena on unloading and reverse loading, we have introduced a *symmetric and unimodular* tensor field

$$\mathbf{A}(\mathbf{X}, t), \quad \mathbf{A} = \mathbf{A}^\top, \quad \det\mathbf{A} = 1,$$

which represents a dimensionless *squared stretch-like* quantity, and assumed that the free energy density ψ_{R} is given by

$$\psi_{\mathrm{R}} = \bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta) + \bar{\psi}^{(2)}(\mathbf{C}, \vartheta) + \bar{\psi}^{(p)}(\mathbf{A}, \vartheta), \tag{1.2}$$

where ϑ is the absolute temperature. Here, $\bar{\psi}^{(1)}$ is an energy associated with intermolecular interactions and modeled using the elastic Cauchy-Green tensor $\mathbf{C}^e = \mathbf{F}^{e\top}\mathbf{F}^e$, $\bar{\psi}^{(2)}$ an energy associated with the stretching of the polymer chains and modeled (as discussed above) using the total Cauchy-Green tensor $\mathbf{C} = \mathbf{F}^\top\mathbf{F}$, and $\bar{\psi}^{(p)}$ a "defect-energy" associated with plastic deformation and introduced via the internal variable $\mathbf{A}$. This last "defect-energy" leads to the development of a *back-stress*, and allows one to phenomenologically account for Bauschinger-like phenomena. In addition, it contributes in an important manner to the plastic source term in the balance of energy.

In a companion paper, Part II, the constitutive theory developed here is further specialized to capture the salient features of the thermo-mechanically coupled strain rate and temperature dependent large deformation mechanical response of a few representative amorphous polymeric materials. The specialized thermo-mechanically coupled theory has been implemented in a finite element program, and the predictive capabilities of the theory and its numerical implementation are validated by comparing the results from a suite of validation experiments of some key macroscopic features, such as the experimentally measured deformed shapes and the load-displacement curves, against corresponding results from numerical simulations.

2   Kinematics

We consider a homogeneous body B identified with the region of space it occupies in a fixed *reference configuration*, and denote by $\mathbf{X}$ an arbitrary material point of B. A *motion* of B is then a smooth one-to-one

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[1] The term "Bauschinger-effect" is used to describe a phenomenon first observed in metals by Bauschinger (1886). He reported that a metal specimen after receiving a certain amount of axial extension into the plastic range, showed a decrease in the magnitude of the yield strength upon subsequent compression. The origins of a Bauschinger-like effect are typically attributed to the generation of internal strains and corresponding stresses during deformation; the causes for such internal stresses are clearly different in polymers from those in metals (for which the term Bauschinger-effect was first coined).

mapping $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ with *deformation gradient, velocity,* and *velocity gradient* given by[2]

$$\mathbf{F} = \nabla\boldsymbol{\chi}, \qquad \mathbf{v} = \dot{\boldsymbol{\chi}}, \qquad \mathbf{L} = \operatorname{grad}\mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \tag{2.1}$$

To model the inelastic response of the amorphous polymeric materials under consideration, we assume that the deformation gradient $\mathbf{F}$ may be multiplicatively decomposed as (Kröner, 1960; Lee, 1969)

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^p. \tag{2.2}$$

As is standard, we assume that

$$J = \det\mathbf{F} > 0,$$

and consistent with this we assume that

$$J^e \stackrel{\text{def}}{=} \det\mathbf{F}^e > 0, \qquad J^p \stackrel{\text{def}}{=} \det\mathbf{F}^p > 0, \tag{2.3}$$

so that $\mathbf{F}^e$ and $\mathbf{F}^p$ are invertible. Here, suppressing the argument t:

- $\mathbf{F}^p(\mathbf{X})$ represents the local inelastic distortion of the material at $\mathbf{X}$ due to a "plastic mechanism" such as the relative chain slippage of the long-chain polymer molecules, or the cumulative effects of destruction of temporary mechanical cross-links. This local deformation carries the material into — and ultimately "pins" the material to — a *coherent structure* that resides in the *structural space*[3] at $\mathbf{X}$ (as represented by the range of $\mathbf{F}^p(\mathbf{X})$);

- $\mathbf{F}^e(\mathbf{X})$ represents the subsequent stretching and rotation of this coherent structure, and thereby represents the corresponding "elastic distortion," such as stretching and rotation of the intermolecular bonds and the long-chain polymer molecules.

We refer to $\mathbf{F}^p$ and $\mathbf{F}^e$ as the *inelastic and elastic distortions.*

By $(2.1)_3$ and (2.2),

$$\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e\mathbf{L}^p\mathbf{F}^{e-1}, \tag{2.4}$$

with

$$\mathbf{L}^e = \dot{\mathbf{F}}^e\mathbf{F}^{e-1}, \qquad \mathbf{L}^p = \dot{\mathbf{F}}^p\mathbf{F}^{p-1}. \tag{2.5}$$

As is standard, we define the total, elastic, and plastic stretching and spin tensors through

$$\left.\begin{aligned}
\mathbf{D} &= \operatorname{sym}\mathbf{L}, & \mathbf{W} &= \operatorname{skw}\mathbf{L}, \\
\mathbf{D}^e &= \operatorname{sym}\mathbf{L}^e, & \mathbf{W}^e &= \operatorname{skw}\mathbf{L}^e, \\
\mathbf{D}^p &= \operatorname{sym}\mathbf{L}^p, & \mathbf{W}^p &= \operatorname{skw}\mathbf{L}^p,
\end{aligned}\right\} \tag{2.6}$$

so that $\mathbf{L} = \mathbf{D} + \mathbf{W}$, $\mathbf{L}^e = \mathbf{D}^e + \mathbf{W}^e$, and $\mathbf{L}^p = \mathbf{D}^p + \mathbf{W}^p$.

The right and left polar decompositions of $\mathbf{F}$ are given by

$$\mathbf{F} = \mathbf{R}\mathbf{U} = \mathbf{V}\mathbf{R}, \tag{2.7}$$

where $\mathbf{R}$ is a rotation (proper orthogonal tensor), while $\mathbf{U}$ and $\mathbf{V}$ are symmetric, positive-definite tensors with

$$\mathbf{U} = \sqrt{\mathbf{F}^\top\mathbf{F}}, \qquad \mathbf{V} = \sqrt{\mathbf{F}\mathbf{F}^\top}. \tag{2.8}$$

Also, the right and left Cauchy-Green tensors are given by

$$\mathbf{C} = \mathbf{U}^2 = \mathbf{F}^\top\mathbf{F}, \qquad \mathbf{B} = \mathbf{V}^2 = \mathbf{F}\mathbf{F}^\top. \tag{2.9}$$

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[2]Notation: We use standard notation of modern continuum mechanics. Specifically: ∇ and Div denote the gradient and divergence with respect to the material point $\mathbf{X}$ in the reference configuration; grad and div denote these operators with respect to the point $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ in the deformed body; a superposed dot denotes the material time-derivative. Throughout, we write $\mathbf{F}^{e-1} = (\mathbf{F}^e)^{-1}$, $\mathbf{F}^{p-\top} = (\mathbf{F}^p)^{-\top}$, etc. We write $\operatorname{tr}\mathbf{A}$, $\operatorname{sym}\mathbf{A}$, $\operatorname{skw}\mathbf{A}$, $\mathbf{A}_0$, and $\operatorname{sym}_0\mathbf{A}$ respectively, for the trace, symmetric, skew, deviatoric, and symmetric-deviatoric parts of a tensor $\mathbf{A}$. Also, the inner product of tensors $\mathbf{A}$ and $\mathbf{B}$ is denoted by $\mathbf{A}\!:\!\mathbf{B}$, and the magnitude of $\mathbf{A}$ by $|\mathbf{A}| = \sqrt{\mathbf{A}\!:\!\mathbf{A}}$.

[3]Also sometimes referred to as the "intermediate" or "relaxed" local space at $\mathbf{X}$.

Similarly, the right and left polar decompositions of $\mathbf{F}^e$ and $\mathbf{F}^p$ are given by

$$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e = \mathbf{V}^e \mathbf{R}^e, \qquad \mathbf{F}^p = \mathbf{R}^p \mathbf{U}^p = \mathbf{V}^p \mathbf{R}^p, \tag{2.10}$$

where $\mathbf{R}^e$ and $\mathbf{R}^p$ are rotations, while $\mathbf{U}^e$, $\mathbf{V}^e$, $\mathbf{U}^p$, $\mathbf{V}^p$ are symmetric, positive-definite tensors with

$$\mathbf{U}^e = \sqrt{\mathbf{F}^{e\top}\mathbf{F}^e}, \qquad \mathbf{V}^e = \sqrt{\mathbf{F}^e\mathbf{F}^{e\top}}, \qquad \mathbf{U}^p = \sqrt{\mathbf{F}^{p\top}\mathbf{F}^p}, \qquad \mathbf{V}^p = \sqrt{\mathbf{F}^p\mathbf{F}^{p\top}}. \tag{2.11}$$

Also, the right and left elastic Cauchy-Green tensors are given by

$$\mathbf{C}^e = \mathbf{U}^{e2} = \mathbf{F}^{e\top}\mathbf{F}^e, \qquad \mathbf{B}^e = \mathbf{V}^{e2} = \mathbf{F}^e\mathbf{F}^{e\top}, \tag{2.12}$$

and the right and left plastic Cauchy-Green tensors are given by

$$\mathbf{C}^p = \mathbf{U}^{p\,2} = \mathbf{F}^{p\top}\mathbf{F}^p, \qquad \mathbf{B}^p = \mathbf{V}^{p\,2} = \mathbf{F}^p\mathbf{F}^{p\top}. \tag{2.13}$$

2.1 Incompressible, irrotational plastic flow

We make two basic kinematical assumptions concerning plastic flow:

(i) First, we make the standard assumption that *plastic flow is incompressible*, so that

$$J^p = \det \mathbf{F}^p = 1 \qquad \text{and} \qquad \operatorname{tr}\mathbf{L}^p = 0. \tag{2.14}$$

Hence, using (2.2) and $(2.14)_1$,

$$J^e = J. \tag{2.15}$$

(ii) Second, from the outset we constrain the theory by limiting our discussion to circumstances under which the material may be idealized as isotropic, cf. §6.3. For isotropic elastic-viscoplastic theories utilizing the Kröner-Lee decomposition it is widely assumed that the plastic flow is *irrotational* in the sense that[4]

$$\mathbf{W}^p = \mathbf{0}. \tag{2.16}$$

Then, trivially, $\mathbf{L}^p \equiv \mathbf{D}^p$ and

$$\dot{\mathbf{F}}^p = \mathbf{D}^p\mathbf{F}^p. \tag{2.17}$$

Thus, using (2.1), (2.4), (2.5), and (2.17), we may write (2.4) for future use as

$$(\nabla \dot{\boldsymbol{\chi}})\mathbf{F}^{-1} = \dot{\mathbf{F}}^e\mathbf{F}^{e-1} + \mathbf{F}^e\,\mathbf{D}^p\,\mathbf{F}^{e-1}. \tag{2.18}$$

3 Frame-indifference

Changes in frame (observer) are smooth time-dependent rigid transformations of the Euclidean space through which the body moves. We require that the theory be invariant under such transformations, and hence under transformations of the form

$$\boldsymbol{\chi}(\mathbf{X}, t) \to \mathbf{Q}(t)(\boldsymbol{\chi}(\mathbf{X}, t) - \mathbf{o}) + \mathbf{y}(t), \tag{3.1}$$

with $\mathbf{Q}(t)$ a rotation (proper-orthogonal tensor), $\mathbf{y}(t)$ a point at each t, and $\mathbf{o}$ a fixed origin. Then, under a change in frame, the deformation gradient transforms according to

$$\mathbf{F} \to \mathbf{Q}\mathbf{F}, \tag{3.2}$$

and hence

$$\mathbf{C} \quad \text{is invariant;} \tag{3.3}$$

also $\dot{\mathbf{F}} \to \mathbf{Q}\dot{\mathbf{F}} + \dot{\mathbf{Q}}\mathbf{F}$, and by $(2.1)_3$,

$$\mathbf{L} \to \mathbf{Q}\mathbf{L}\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top. \tag{3.4}$$

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[4]Cf. Gurtin and Anand (2005) for a detailed discussion concerning irrotationality of plastic flow for isotropic materials.

Thus,
$$\mathbf{D} \to \mathbf{Q}\mathbf{D}\mathbf{Q}^\top, \qquad \mathbf{W} \to \mathbf{Q}\mathbf{W}\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top . \tag{3.5}$$

Moreover, $\mathbf{F}^e\mathbf{F}^p \to \mathbf{Q}\mathbf{F}^e\mathbf{F}^p$, and therefore, since *observers view only the deformed configuration*,

$$\mathbf{F}^e \to \mathbf{Q}\mathbf{F}^e, \qquad \mathbf{F}^p \text{ is invariant,} \tag{3.6}$$

and, by (2.5),
$$\mathbf{L}^e \to \mathbf{Q}\mathbf{L}^e\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top, \tag{3.7}$$

and
$$\mathbf{L}^p, \ \mathbf{D}^p, \ \text{and} \ \mathbf{W}^p \ \text{are invariant.} \tag{3.8}$$

Further, by (2.10),

$$\mathbf{F}^e = \mathbf{R}^e\mathbf{U}^e \to \mathbf{Q}\mathbf{F}^e = \underline{\mathbf{Q}\mathbf{R}^e}\,\mathbf{U}^e,$$

$$\mathbf{F}^e = \mathbf{V}^e\mathbf{R}^e \to \mathbf{Q}\mathbf{F}^e = \underline{\mathbf{Q}\mathbf{V}^e\mathbf{Q}^\top}\,\mathbf{Q}\mathbf{R}^e,$$

and we may conclude from the uniqueness of the polar decomposition that

$$\mathbf{R}^e \to \mathbf{Q}\mathbf{R}^e, \qquad \mathbf{V}^e \to \mathbf{Q}\mathbf{V}^e\mathbf{Q}^\top, \qquad \mathbf{U}^e \text{ is invariant.} \tag{3.9}$$

Hence, from (2.12), $\mathbf{B}^e$ and $\mathbf{C}^e$ transform as

$$\mathbf{B}^e \to \mathbf{Q}\mathbf{B}^e\mathbf{Q}^\top, \qquad \text{and} \qquad \mathbf{C}^e \text{ is invariant;} \tag{3.10}$$

further, since $\mathbf{F}^p$ is invariant,
$$\mathbf{B}^p \qquad \text{and} \qquad \mathbf{C}^p \text{ are also invariant.} \tag{3.11}$$

4   Development of the theory based on the principle of virtual power

Following Gurtin (2000), Anand and Gurtin (2003), and Gurtin and Anand (2005), we develop the theory based on the principle of virtual power.

We denote by P an arbitrary *part* (subregion) of the reference body B with $\mathbf{n}$ the outward unit normal on the boundary ∂P of P. The power expended on P by material or bodies exterior to P results from a *macroscopic surface traction* $\mathbf{s}(\mathbf{n})$, measured per unit area in the reference body, and a *macroscopic body force* $\mathbf{b}_{\mathrm{R}}$, measured per unit volume in the reference body, each of whose working accompanies the macroscopic motion of the body; the body force $\mathbf{b}_{\mathrm{R}}$ presumed to account for inertia; that is, granted the underlying frame is inertial,

$$\mathbf{b}_{\mathrm{R}} = \mathbf{b}_{0\mathrm{R}} - \rho_{\mathrm{R}}\ddot{\boldsymbol{\chi}}, \tag{4.1}$$

with $\mathbf{b}_{0\mathrm{R}}$ the non-inertial body force and ρ_{R} the mass density in the reference configuration. We therefore write the *external power* as

$$\mathcal{W}_{\mathrm{ext}}(\mathrm{P}) = \int_{\partial \mathrm{P}} \mathbf{s}(\mathbf{n}) \cdot \dot{\boldsymbol{\chi}}\, dA + \int_{\mathrm{P}} \mathbf{b}_{\mathrm{R}} \cdot \dot{\boldsymbol{\chi}}\, dV. \tag{4.2}$$

We assume that power is expended internally by a stress $\mathbf{P}$ power-conjugate to $\dot{\mathbf{F}}$, an *elastic stress* $\mathbf{T}^e$ power-conjugate to $\dot{\mathbf{F}}^e$, and *plastic stress* $\mathbf{T}^p$ power-conjugate to $\mathbf{D}^p$, and we write the *internal power* as

$$\mathcal{W}_{\mathrm{int}}(\mathrm{P}) = \int_{\mathrm{P}} (\mathbf{P} : \dot{\mathbf{F}} + \mathbf{T}^e : \dot{\mathbf{F}}^e + \mathbf{T}^p : \mathbf{D}^p)\, dV. \tag{4.3}$$

Here $\mathbf{P}$, $\mathbf{T}^e$, $\mathbf{T}^p$ are defined over the body for all time. We assume that $\mathbf{T}^p$ is *symmetric deviatoric*, since $\mathbf{D}^p$ is symmetric deviatoric.

Remark 1: In a previously-developed theory for amorphous polymeric materials (Anand and Gurtin, 2003), which was also based on the principle of virtual power, a term similar to $\mathbf{P}:\dot{\mathbf{F}}$ does not appear in the expression for the internal power. This term in the internal power is introduced here to account for the underlying rubber-like, non-linear elastic response dependent on the the total deformation gradient $\mathbf{F}$ from the reference configuration. The contribution to the macroscopic stress from such a term starts to dominate at moderate to large deformations.

Principle of virtual power

Assume that, at some arbitrarily chosen but *fixed time*, the fields $\boldsymbol{\chi}$, $\mathbf{F}^e$ (and hence $\mathbf{F}$ and $\mathbf{F}^p$) are known, and consider the fields $\dot{\boldsymbol{\chi}}$, $\dot{\mathbf{F}}^e$, and $\mathbf{D}^p$ as virtual velocities to be specified independently in a manner consistent with the constraint (2.18). That is, denoting the virtual fields by $\tilde{\boldsymbol{\chi}}$, $\tilde{\dot{\mathbf{F}}}^e$, and $\tilde{\mathbf{D}}^p$ to differentiate them from fields associated with the actual evolution of the body, we require that

$$(\nabla\tilde{\boldsymbol{\chi}})\mathbf{F}^{-1} = \tilde{\dot{\mathbf{F}}}^e\mathbf{F}^{e-1} + \mathbf{F}^e\,\tilde{\mathbf{D}}^p\,\mathbf{F}^{e-1}. \tag{4.4}$$

More specifically, we define a *generalized virtual velocity* to be a list

$$\mathcal{V} = (\tilde{\dot{\boldsymbol{\chi}}}, \tilde{\dot{\mathbf{F}}}^e, \tilde{\mathbf{D}}^p),$$

consistent with (4.4). Then, writing

$$\left.\begin{aligned}
\mathcal{W}_{\text{ext}}(\text{P}, \mathcal{V}) &= \int_{\partial\text{P}} \mathbf{s}(\mathbf{n})\cdot\tilde{\dot{\boldsymbol{\chi}}}\,dA + \int_{\text{P}} \mathbf{b}_{\text{R}}\cdot\tilde{\dot{\boldsymbol{\chi}}}dV, \\
\mathcal{W}_{\text{int}}(\text{P}, \mathcal{V}) &= \int_{\text{P}} \left(\mathbf{P}:\nabla\tilde{\dot{\boldsymbol{\chi}}} + \mathbf{T}^e:\tilde{\dot{\mathbf{F}}}^e + \mathbf{T}^p:\tilde{\mathbf{D}}^p\right) dV,
\end{aligned}\right\} \tag{4.5}$$

respectively, for the external and internal expenditures of *virtual power*, the *principle of virtual power* is the requirement that the external and internal powers be balanced. That is, given any part P,

$$\mathcal{W}_{\text{ext}}(\text{P}, \mathcal{V}) = \mathcal{W}_{\text{int}}(\text{P}, \mathcal{V}) \quad \text{for all generalized virtual velocities } \mathcal{V}. \tag{4.6}$$

Frame-indifference of the internal power and its consequences

We assume that the internal power $\mathcal{W}_{\text{int}}(\text{P}, \mathcal{V})$ is invariant under a change in frame and that the virtual fields transform in a manner identical to their nonvirtual counterparts. Then given a change in frame, invariance of the internal power requires that

$$\mathcal{W}^*(\text{P}, \mathcal{V}^*) = \mathcal{W}(\text{P}, \mathcal{V}), \tag{4.7}$$

where $\mathcal{V}^*$ is the generalized virtual velocity in the new frame. In the new frame the stresses $\mathbf{P}$, $\mathbf{T}^e$ and $\mathbf{T}^p$ transform to $\mathbf{P}^*$, $\mathbf{T}^{e*}$, and $\mathbf{T}^{p*}$, while $\nabla\tilde{\dot{\boldsymbol{\chi}}}$ and $\tilde{\dot{\mathbf{F}}}^e$ transform to

$$(\nabla\tilde{\dot{\boldsymbol{\chi}}})^* = \mathbf{Q}\nabla\tilde{\dot{\boldsymbol{\chi}}} + \dot{\mathbf{Q}}\nabla\boldsymbol{\chi}, \qquad (\tilde{\dot{\mathbf{F}}}^e)^* = \mathbf{Q}\tilde{\dot{\mathbf{F}}}^e + \dot{\mathbf{Q}}\mathbf{F}^e,$$

and $\tilde{\mathbf{D}}^p$ is invariant. Thus, under a change in frame $\mathcal{W}_{\text{int}}(\text{P}, \mathcal{V})$ transforms to

$$\mathcal{W}^*_{\text{int}}(\text{P}, \mathcal{V}^*) = \int_{\text{P}} \left(\mathbf{P}^*:(\mathbf{Q}\nabla\tilde{\dot{\boldsymbol{\chi}}} + \dot{\mathbf{Q}}\nabla\boldsymbol{\chi}) + \mathbf{T}^{e*}:\left(\mathbf{Q}\tilde{\dot{\mathbf{F}}}^e + \dot{\mathbf{Q}}\mathbf{F}^e\right) + \mathbf{T}^{p*}:\tilde{\mathbf{D}}^p\right) dV$$

$$= \int_{\text{P}} \left(\mathbf{Q}^{\top}\mathbf{P}^*:(\nabla\tilde{\dot{\boldsymbol{\chi}}} + \mathbf{Q}^{\top}\dot{\mathbf{Q}}\nabla\boldsymbol{\chi}) + \mathbf{Q}^{\top}\mathbf{T}^{e*}:\left(\tilde{\dot{\mathbf{F}}}^e + \mathbf{Q}^{\top}\dot{\mathbf{Q}}\mathbf{F}^e\right) + \mathbf{T}^{p*}:\tilde{\mathbf{D}}^p\right) dV.$$

Then (4.7) implies that

$$\int_{\text{P}} \left(\mathbf{Q}^{\top}\mathbf{P}^*:(\nabla\tilde{\dot{\boldsymbol{\chi}}} + \mathbf{Q}^{\top}\dot{\mathbf{Q}}\nabla\boldsymbol{\chi}) + \mathbf{Q}^{\top}\mathbf{T}^{e*}:\left(\tilde{\dot{\mathbf{F}}}^e + \mathbf{Q}^{\top}\dot{\mathbf{Q}}\mathbf{F}^e\right) + \mathbf{T}^{p*}:\tilde{\mathbf{D}}^p\right) dV$$

$$= \int_{\text{P}}(\mathbf{P}:\nabla\tilde{\dot{\boldsymbol{\chi}}} + \mathbf{T}^e:\tilde{\dot{\mathbf{F}}}^e + \mathbf{T}^p:\tilde{\mathbf{D}}^p)\,dV, \tag{4.8}$$

or equivalently, since the part P is arbitrary,

$$\mathbf{Q}^\top\mathbf{P}^*:(\nabla\tilde{\boldsymbol{\chi}}+\mathbf{Q}^\top\dot{\mathbf{Q}}\nabla\boldsymbol{\chi})+\mathbf{Q}^\top\mathbf{T}^{e*}:\left(\dot{\tilde{\mathbf{F}}}^e+\mathbf{Q}^\top\dot{\mathbf{Q}}\mathbf{F}^e\right)+\mathbf{T}^{p*}:\tilde{\mathbf{D}}^p=\mathbf{P}:\nabla\tilde{\boldsymbol{\chi}}+\mathbf{T}^e:\dot{\tilde{\mathbf{F}}}^e+\mathbf{T}^p:\tilde{\mathbf{D}}^p. \qquad (4.9)$$

Also, since the change in frame is arbitrary, if we choose it such that $\mathbf{Q}$ is an arbitrary *time-independent* rotation, so that $\dot{\mathbf{Q}}=\mathbf{0}$, we find from (4.9) that

$$\left((\mathbf{Q}^\top\mathbf{P}^*)-\mathbf{P}\right):\nabla\tilde{\boldsymbol{\chi}}+\left((\mathbf{Q}^\top\mathbf{T}^{e*})-\mathbf{T}^e\right):\dot{\tilde{\mathbf{F}}}^e+\left(\mathbf{T}^{p*}-\mathbf{T}^p\right):\tilde{\mathbf{D}}^p=0\,.$$

Since this must hold for all $\nabla\tilde{\boldsymbol{\chi}}$, $\dot{\tilde{\mathbf{F}}}^e$, and $\tilde{\mathbf{D}}^p$, we find that the stresses $\mathbf{P}$ and $\mathbf{T}^e$ transform according to

$$\mathbf{P}^*=\mathbf{QP},\qquad \mathbf{T}^{e*}=\mathbf{QT}^e, \qquad (4.10)$$

while $\mathbf{T}^p$ is invariant

$$\mathbf{T}^{p*}=\mathbf{T}^p. \qquad (4.11)$$

Next, if we assume that $\mathbf{Q}=\mathbf{1}$ at the time in question and that $\dot{\mathbf{Q}}$ is an arbitrary skew tensor, we find from (4.9), using (4.10), (4.11) and recalling $\mathbf{F}=\nabla\boldsymbol{\chi}$, that

$$(\mathbf{PF}^\top):\dot{\mathbf{Q}}+(\mathbf{T}^e\mathbf{F}^{e\top}):\dot{\mathbf{Q}}=0,$$

or that the tensors $(\mathbf{PF}^\top)$ and $(\mathbf{T}^e\mathbf{F}^{e\top})$ are *symmetric*,

$$\mathbf{PF}^\top=\mathbf{FP}^\top,\qquad \mathbf{T}^e\mathbf{F}^{e\top}=\mathbf{F}^e\mathbf{T}^{e\top}\,. \qquad (4.12)$$

Macroscopic force balance

In applying the virtual balance (4.6) we are at liberty to choose any $\mathcal{V}$ consistent with the constraint (4.4). Consider a generalized virtual velocity with $\tilde{\mathbf{D}}^p\equiv\mathbf{0}$, so that

$$\dot{\tilde{\mathbf{F}}}^e=(\nabla\tilde{\boldsymbol{\chi}})\mathbf{F}^{p-1}. \qquad (4.13)$$

For this choice of $\mathcal{V}$, (4.6) yields

$$\int_{\partial\mathrm{P}}\mathbf{s}(\mathbf{n})\cdot\tilde{\boldsymbol{\chi}}\,dA+\int_{\mathrm{P}}\mathbf{b}_\mathrm{R}\cdot\tilde{\boldsymbol{\chi}}\,dV=\int_{\mathrm{P}}\left(\mathbf{P}+\mathbf{T}^e\mathbf{F}^{p-\top}\right):\nabla\tilde{\boldsymbol{\chi}}\,dV. \qquad (4.14)$$

Thus by defining

$$\mathbf{T}_\mathrm{R}\overset{\mathrm{def}}{=}\mathbf{P}+\mathbf{T}^e\mathbf{F}^{p-\top}, \qquad (4.15)$$

and using the divergence theorem, we may conclude that

$$\int_{\partial\mathrm{P}}\left(\mathbf{s}(\mathbf{n})-\mathbf{T}_\mathrm{R}\mathbf{n}\right)\cdot\tilde{\boldsymbol{\chi}}\,dA+\int_{\mathrm{P}}(\mathrm{Div}\,\mathbf{T}_\mathrm{R}+\mathbf{b}_\mathrm{R})\cdot\tilde{\boldsymbol{\chi}}\,dV=0.$$

Since this relation must hold for all P and all $\tilde{\boldsymbol{\chi}}$, standard variational arguments yield the traction condition

$$\mathbf{s}(\mathbf{n})=\mathbf{T}_\mathrm{R}\mathbf{n}\,, \qquad (4.16)$$

and the local macroscopic force balance

$$\mathrm{Div}\,\mathbf{T}_\mathrm{R}+\mathbf{b}_\mathrm{R}=\mathbf{0}, \qquad (4.17)$$

respectively. Moreover, (4.12) and (4.15) imply that

$$\mathbf{T}_\mathrm{R}\mathbf{F}^\top=\mathbf{FT}_\mathrm{R}^\top. \qquad (4.18)$$

Thus $\mathbf{T}_\mathrm{R}$ plays the role of the classical *Piola stress*, and (4.17) and (4.18) represent the local *macroscopic force and moment balances* in the reference configuration. Since the body force $\mathbf{b}_\mathrm{R}$ has been presumed to account for inertia, so that (4.1) is satisfied, (4.17) reduces to the local balance law for linear momentum:

$$\mathrm{Div}\,\mathbf{T}_\mathrm{R}+\mathbf{b}_{0\mathrm{R}}=\rho_\mathrm{R}\ddot{\boldsymbol{\chi}}, \qquad (4.19)$$

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with $\mathbf{b}_{0\mathrm{R}}$ the noninertial body force.

Further, as is standard, the Piola stress $\mathbf{T}_{\mathrm{R}}$ is related to the symmetric Cauchy stress $\mathbf{T}$ in the deformed body by

$$\mathbf{T}_{\mathrm{R}} = J\mathbf{T}\mathbf{F}^{-\top}. \tag{4.20}$$

Thus,

$$\mathbf{T} = J^{-1}\mathbf{T}_{\mathrm{R}}\mathbf{F}^{\top}, \tag{4.21}$$

and using (2.15) and $\mathbf{F}^{e\top} = \mathbf{F}^{p-\top}\mathbf{F}^{\top}$, in (4.15) yields that the Cauchy stress admits the additive decomposition

$$\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)}, \tag{4.22}$$

where

$$\mathbf{T}^{(1)} \stackrel{\text{def}}{=} J^{-1}\mathbf{T}^{e}\mathbf{F}^{e\top} \qquad \text{and} \qquad \mathbf{T}^{(2)} \stackrel{\text{def}}{=} J^{-1}\mathbf{P}\mathbf{F}^{\top} \tag{4.23}$$

are symmetric since $\mathbf{T}$ is symmetric.

Microscopic force balance

To discuss the microscopic counterparts of the macroscopic force balance, consider a generalized virtual velocity with

$$\tilde{\dot{\chi}} \equiv \mathbf{0}; \tag{4.24}$$

also, choose the virtual field $\tilde{\mathbf{D}}^{p}$ arbitrarily, and let

$$\tilde{\mathbf{F}}^{e} = -\mathbf{F}^{e}\tilde{\mathbf{D}}^{p}, \tag{4.25}$$

consistent with (4.4). Thus

$$\mathbf{T}^{e} : \tilde{\dot{\mathbf{F}}}^{e} = -(\mathbf{F}^{e\top}\mathbf{T}^{e}) : \tilde{\mathbf{D}}^{p}. \tag{4.26}$$

Next, define a *Mandel stress* by

$$\mathbf{M}^{e} \stackrel{\text{def}}{=} \mathbf{F}^{e\top}\mathbf{T}^{e} = J\mathbf{F}^{e\top}\mathbf{T}^{(1)}\mathbf{F}^{e-\top}, \tag{4.27}$$

which in general is not symmetric. Then, on account of our choice (4.24) the external power vanishes, so that, by (4.6), the internal power must also vanish, and satisfy

$$\mathcal{W}_{\mathrm{int}}(\mathrm{P}, \mathcal{V}) = \int_{\mathrm{P}} \left(\mathbf{T}^{p} - \mathbf{M}^{e} \right) : \tilde{\mathbf{D}}^{p} \, dV = 0.$$

Since this must be satisfied for all P and all symmetric and deviatoric tensors $\tilde{\mathbf{D}}^{p}$, a standard argument yields the *microforce balance*

$$\mathrm{sym}_{0}\mathbf{M}^{e} = \mathbf{T}^{p}. \tag{4.28}$$

This microscopic balance characterizes the interaction between internal forces associated with the elastic and plastic response of the material.

5   Balance of energy. Entropy imbalance. Free-energy imbalance

Let

- $\vartheta > 0$ denote the absolute temperature;

- ε_{R} and η_{R} represent the *internal energy* and *entropy* densities, measured per unit volume in the reference body;

- $\mathbf{q}_{\mathrm{R}}$ denote the *heat flux*, measured per unit area in the reference body; and

- q_{R} denote the scalar heat supply, measured per unit volume in the reference body.

Then (cf., e.g., Truesdell and Noll, 1965), *balance of energy* is the requirement that

$$\overline{\int_{\mathrm{P}} \dot{\varepsilon}_{\mathrm{R}} \, dV} = -\int_{\partial \mathrm{P}} \mathbf{q}_{\mathrm{R}} \cdot \mathbf{n} \, dA + \int_{\mathrm{P}} q_{\mathrm{R}} \, dV + \mathcal{W}_{\mathrm{ext}}(\mathrm{P}), \tag{5.1}$$

while the *second law* takes the form of an *entropy imbalance*

$$\overline{\int_{\mathrm{P}} \dot{\eta}_{\mathrm{R}} \, dV} \geq -\int_{\partial \mathrm{P}} \frac{\mathbf{q}_{\mathrm{R}} \cdot \mathbf{n}}{\vartheta} \, dA + \int_{\mathrm{P}} \frac{q_{\mathrm{R}}}{\vartheta} \, dV. \tag{5.2}$$

Thus, since $\mathcal{W}_{\mathrm{ext}}(\mathrm{P}) = \mathcal{W}_{\mathrm{int}}(\mathrm{P})$ and since P is arbitrary, we may use (4.3) to obtain local forms of (5.1) and (5.2):

$$\left. \begin{aligned} \dot{\varepsilon}_{\mathrm{R}} &= -\mathrm{Div}\,\mathbf{q}_{\mathrm{R}} + q_{\mathrm{R}} + \mathbf{P} : \dot{\mathbf{F}} + \mathbf{T}^e : \dot{\mathbf{F}}^e + \mathbf{T}^p : \mathbf{D}^p, \\ \dot{\eta}_{\mathrm{R}} &\geq -\frac{1}{\vartheta}\mathrm{Div}\,\mathbf{q}_{\mathrm{R}} + \frac{1}{\vartheta^2}\mathbf{q}_{\mathrm{R}} \cdot \nabla\vartheta + \frac{q_{\mathrm{R}}}{\vartheta} \,. \end{aligned} \right\} \tag{5.3}$$

Let

$$\psi_{\mathrm{R}} \stackrel{\mathrm{def}}{=} \varepsilon_{\mathrm{R}} - \vartheta\eta_{\mathrm{R}} \tag{5.4}$$

denote the *(Helmholtz) free energy* per unit volume of the reference body. Then (5.3) yields the *local free-energy imbalance*

$$\dot{\psi}_{\mathrm{R}} + \eta_{\mathrm{R}}\dot{\vartheta} + \frac{1}{\vartheta}\,\mathbf{q}_{\mathrm{R}} \cdot \nabla\vartheta - \mathbf{P} : \dot{\mathbf{F}} - \mathbf{T}^e : \dot{\mathbf{F}}^e - \mathbf{T}^p : \mathbf{D}^p \leq 0 \,. \tag{5.5}$$

Two new stress measures

Note that neither of the conjugate stress and deformation rate pairs $(\mathbf{P}, \dot{\mathbf{F}})$ and $(\mathbf{T}^e, \dot{\mathbf{F}}^e)$ appearing in (5.5) are invariant under a change in frame. Accordingly, in this section we introduce two new stresses; these stresses allow us to express the balance of internal energy and the free-energy imbalance in forms which are more amenable to applications.

From (4.23),

$$\mathbf{T}^e = J\mathbf{T}^{(1)}\mathbf{F}^{e-\top} \qquad \text{and} \qquad \mathbf{P} = J\mathbf{T}^{(2)}\mathbf{F}^{-\top}. \tag{5.6}$$

We introduce two new stress measures

$$\mathbf{S}^e \stackrel{\mathrm{def}}{=} \mathbf{F}^{e-1}\mathbf{T}^e = J\,\mathbf{F}^{e-1}\mathbf{T}^{(1)}\mathbf{F}^{e-\top} \qquad \text{and} \qquad \mathbf{S} \stackrel{\mathrm{def}}{=} \mathbf{F}^{-1}\mathbf{P} = J\,\mathbf{F}^{-1}\mathbf{T}^{(2)}\mathbf{F}^{-\top}, \tag{5.7}$$

which are symmetric, since $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$ are symmetric. Thus $\mathbf{S}$ represents a second Piola stress with respect to the reference space, and $\mathbf{S}^e$ represents a second Piola stress with respect to the intermediate structural space. Note that by using the definition $(5.7)_1$, the Mandel stress defined in (4.27) is related to the stress measure $\mathbf{S}^e$ by

$$\mathbf{M}^e = \mathbf{C}^e\mathbf{S}^e. \tag{5.8}$$

Next, differentiating $(2.9)_1$ results in the following expression for the rate of change of $\mathbf{C}$,

$$\dot{\mathbf{C}} = \mathbf{F}^\top\dot{\mathbf{F}} + \dot{\mathbf{F}}^\top\mathbf{F}.$$

Hence, since $\mathbf{S}$ is symmetric,

$$\mathbf{S} : \dot{\mathbf{C}} = 2\,\mathbf{S} : \mathbf{F}^\top\dot{\mathbf{F}} = 2\,(\mathbf{F}\mathbf{S}) : \dot{\mathbf{F}},$$

or, using $(5.7)_2$, we obtain

$$\mathbf{P} : \dot{\mathbf{F}} = \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}}. \tag{5.9}$$

In an entirely analogous manner,

$$\mathbf{T}^e : \dot{\mathbf{F}}^e = \frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e. \tag{5.10}$$

Then, from (4.3), (5.9) and (5.10), we note that the internal power per unit volume of the reference body is

$$\frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e + \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} + \mathbf{T}^p : \mathbf{D}^p \,. \tag{5.11}$$

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Thus, the energy balance $(5.3)_1$ may be written as

$$\dot{\varepsilon}_{\mathrm{R}} = -\operatorname{Div}\mathbf{q}_{\mathrm{R}} + q_{\mathrm{R}} + \frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e + \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} + \mathbf{T}^p : \mathbf{D}^p, \tag{5.12}$$

while the free-energy imbalance (5.5) becomes

$$\dot{\psi}_{\mathrm{R}} + \eta_{\mathrm{R}}\dot{\vartheta} + \frac{1}{\vartheta}\,\mathbf{q}_{\mathrm{R}} \cdot \nabla\vartheta - \frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e - \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} - \mathbf{T}^p : \mathbf{D}^p \leq 0. \tag{5.13}$$

Finally, we note that ψ_{R}, η_{R} and ϑ are invariant under a change in frame since they are scalar fields, and on account of the transformation rules discussed in section 3, the transformation rules (4.10) and (4.11), and the definitions (4.27) and (5.7), the fields

$$\mathbf{C}, \quad \mathbf{C}^e, \quad \mathbf{B}^p, \quad \mathbf{D}^p, \quad \mathbf{S}, \quad \mathbf{S}^e, \quad \mathbf{T}^p, \quad \text{and} \quad \mathbf{M}^e, \tag{5.14}$$

are also invariant, as are the fields

$$\mathbf{q}_{\mathrm{R}}, \quad \nabla\vartheta, \tag{5.15}$$

since they are referential vector fields.

6 Constitutive theory

To account for the major strain-hardening and softening characteristics of polymeric materials observed during plastic deformation, we introduce macroscopic *internal variables* to represent important aspects of the microstructural resistance to plastic flow. Specifically we introduce

- A list of m scalar *internal state-variables*

$$\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_m).$$

  Since $\boldsymbol{\xi}$ are scalar fields they are invariant under a change in frame.

- A *symmetric and unimodular* tensor field

$$\mathbf{A}(\mathbf{X}, t), \quad \mathbf{A} = \mathbf{A}^\top, \quad \det\mathbf{A} = 1,$$

  which represents a dimensionless *squared stretch-like* quantity, which as a linear transformation, maps vectors in the intermediate space, into vectors in the same space. Thus, $\mathbf{A}$ is a *structural tensor*,[5] and therefore invariant under a change in frame.

Guided by the free-energy imbalance (5.13), and by experience with previous constitutive theories for amorphous polymeric materials (cf., e.g., Anand and Gurtin, 2003), we assume the following *special* set of constitutive equations:[6]

$$\left.\begin{aligned} \psi_{\mathrm{R}} &= \bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta) + \bar{\psi}^{(2)}(\mathbf{C}, \vartheta) + \bar{\psi}^{(p)}(\mathbf{A}, \vartheta), \\[4pt] \eta_{\mathrm{R}} &= \bar{\eta}^{(1)}(\mathbf{C}^e, \vartheta) + \bar{\eta}^{(2)}(\mathbf{C}, \vartheta) + \bar{\eta}^{(p)}(\mathbf{A}, \vartheta), \\[4pt] \mathbf{S}^e &= \bar{\mathbf{S}}^e(\mathbf{C}^e, \vartheta), \\[4pt] \mathbf{S} &= \bar{\mathbf{S}}(\,\mathbf{C},\ \vartheta), \\[4pt] \mathbf{T}^p &= \bar{\mathbf{T}}^p(\mathbf{D}^p, \boldsymbol{\Lambda}), \\[4pt] \dot{\xi}_i &= h_i(\mathbf{D}^p, \boldsymbol{\Lambda}), \\[4pt] \dot{\mathbf{A}} &= \mathbf{D}^p\mathbf{A} + \mathbf{A}\mathbf{D}^p - \mathbf{G}(\boldsymbol{\Lambda})d^p, \qquad d^p \stackrel{\text{def}}{=} |\mathbf{D}^p|, \end{aligned}\right\} \tag{6.1}$$

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[5]That is, a tensor defined in the intermediate space.

[6]We do not seek the most general constitutive equations consistent with (5.13), in which each constitutive function contains all the various kinematic and internal variables appearing in (6.1).

where $\mathbf{\Lambda}$ denotes the list

$$\mathbf{\Lambda} = (\mathbf{C}^e, \mathbf{B}^p, \mathbf{A}, \boldsymbol{\xi}, \vartheta). \tag{6.2}$$

To the constitutive equations (6.1), we append a simple Fourier's relation for the heat flux,

$$\mathbf{q}_{\mathrm{R}} = -\mathbf{K}(\vartheta) \, \nabla \vartheta \,, \tag{6.3}$$

where $\mathbf{K}$ is a positive definite thermal conductivity. Note that on account of the transformation rules listed in the paragraph containing (5.14) and (5.15) and since $(\boldsymbol{\xi}, \mathbf{A})$ are also invariant, *the constitutive equations* (6.1) *and* (6.3) *are frame-indifferent.*

In $(6.1)_1$, $\bar{\psi}^{(1)}$ is an energy associated with intermolecular interactions and modeled using the elastic Cauchy-Green tensor $\mathbf{C}^e = \mathbf{F}^{e\top}\mathbf{F}^e$, $\bar{\psi}^{(2)}$ an energy associated with the stretching of the polymer chains and modeled using the total Cauchy-Green tensor $\mathbf{C} = \mathbf{F}^\top \mathbf{F}$, and $\bar{\psi}^{(p)}$ a "defect-energy" associated with plastic deformation and introduced via the internal variable $\mathbf{A}$. This last defect-energy leads to the development of a *back-stress*, and allows one to phenomenologically account for Bauschinger-like phenomena on unloading and reverse loading. In the evolution equation $(6.1)_7$ for $\mathbf{A}$, the term $\mathbf{G}(\mathbf{\Lambda}) \, d^p$ represents a *dynamic recovery* term. If this dynamic recovery term were to vanish, then we may associate $\mathbf{A}$ with the left Cauchy-Green tensor $\mathbf{B}^p = \mathbf{F}^p \mathbf{F}^{p\top}$, since then, for a constitutive theory with $\mathbf{W}^p = \mathbf{0}$,

$$\dot{\mathbf{B}}^p = \mathbf{D}^p \mathbf{B}^p + \mathbf{B}^p \mathbf{D}^p. \tag{6.4}$$

In the theory developed here, as in the classical small deformation theory of metal plasticity with non-linear kinematic-hardening (Armstrong and Frederick, 1966), we allow for *dynamic recovery*, that is we allow for $\mathbf{G}(\mathbf{\Lambda}) \neq \mathbf{0}$, and thus in general $\mathbf{A}$ is not the same as $\mathbf{B}^p$. Since $\det \mathbf{A} = 1$, the evolution equation $(6.1)_7$ for $\mathbf{A}$ must satisfy $\operatorname{tr}(\dot{\mathbf{A}}\mathbf{A}^{-1}) = 0$, and hence the recovery function $\mathbf{G}(\mathbf{\Lambda})$ is constrained to satisfy $\operatorname{tr}(\mathbf{G}(\mathbf{\Lambda})\mathbf{A}^{-1}) = 0$. The evolution equation $(6.1)_7$ represents a generalization of the non-linear kinematic-hardening rule (Armstrong and Frederick, 1966) of the small deformation theory of classical metal viscoplasticity,[7] but here applied to polymer-viscoplasticity.

Remark 2: The evolution equation for $\mathbf{A}$ may be further generalized to read

$$\dot{\mathbf{A}} = \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\mathbf{\Lambda}) d^p - \mathbf{G}_{\mathrm{static}}(\mathbf{\Lambda}),$$

where the third term on the right represents *static recovery* (or time recovery, or thermal recovery), since it does not depend on $\mathbf{D}^p$. It is a simple matter to include such a static recovery term, but we refrain from doing this here as it does not add to the central issue of the mathematical development of the theory in this paper.

Remark 3: The introduction of the tensor $\mathbf{A}$ to account for a defect energy associated with plastic deformation is similar to introducing a dependence of the free energy on $\mathbf{B}_{\mathrm{en}}^p = \mathbf{F}_{\mathrm{en}}^p \mathbf{F}_{\mathrm{en}}^{p\,\top}$, where $\mathbf{F}_{\mathrm{en}}^p$ is an "energetic" part of $\mathbf{F}^p$ introduced via a decomposition $\mathbf{F}^p = \mathbf{F}_{\mathrm{en}}^p \mathbf{F}_{\mathrm{dis}}^p$ by Lion (2000). For a detailed discussion of the relationship of $\mathbf{A}$ to $\mathbf{B}_{\mathrm{en}}^p$ see Henann and Anand (2008).

6.1 Thermodynamic restrictions

From $(6.1)_1$

$$\dot{\psi}_{\mathrm{R}} = \frac{\partial \bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta)}{\partial \mathbf{C}^e} : \dot{\mathbf{C}}^e + \frac{\partial \bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta)}{\partial \vartheta} \dot{\vartheta} + \frac{\partial \bar{\psi}^{(2)}(\mathbf{C}, \vartheta)}{\partial \mathbf{C}} : \dot{\mathbf{C}} + \frac{\partial \bar{\psi}^{(2)}(\mathbf{C}, \vartheta)}{\partial \vartheta} \dot{\vartheta}$$
$$+ \frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \dot{\mathbf{A}} + \frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \vartheta} \dot{\vartheta},$$

and, using $(6.1)_7$ and the symmetry of $\mathbf{A}$ and $\partial \bar{\psi} / \partial \mathbf{A}$,

$$\frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \dot{\mathbf{A}} = \frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \left(\mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\mathbf{\Lambda}) \, d^p \right)$$
$$= 2 \left(\frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} \mathbf{A} \right)_0 : \mathbf{D}^p - \left(\frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \mathbf{G}(\mathbf{\Lambda}) \right) d^p.$$

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[7]Cf., e.g., Chaboche (2008) for a recent review of the large variety of kinematic-hardening rules in classical small deformation metal-viscoplasticity.

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Hence, satisfaction of the free-energy imbalance (5.13) requires that the constitutive equations (6.1) and (6.3) satisfy

$$\left(\frac{1}{2}\bar{\mathbf{S}}^e(\mathbf{C}^e,\vartheta)-\frac{\partial\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\mathbf{C}^e}\right):\dot{\mathbf{C}}^e+\left(\frac{1}{2}\bar{\mathbf{S}}(\mathbf{C},\vartheta)-\frac{\partial\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\mathbf{C}}\right):\dot{\mathbf{C}}$$

$$-\left(\bar{\eta}^{(1)}(\mathbf{C}^e,\vartheta)+\frac{\partial\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\vartheta}\right)\dot{\vartheta}-\left(\bar{\eta}^{(2)}(\mathbf{C},\vartheta)+\frac{\partial\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\vartheta}\right)\dot{\vartheta}-\left(\bar{\eta}^{(p)}(\mathbf{A},\vartheta)+\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\vartheta}\right)\dot{\vartheta}$$

$$+\left(\bar{\mathbf{T}}^p(\mathbf{D}^p,\mathbf{\Lambda})-2\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\right)_0\right):\mathbf{D}^p+\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}:\mathbf{G}(\mathbf{\Lambda})\right)d^p+\frac{1}{\vartheta}\,\nabla\vartheta\cdot\mathbf{K}(\vartheta)\nabla\vartheta\geq 0,\qquad(6.5)$$

and hold for all arguments in the domains of the constitutive functions, and in all motions of the body. Thus, *sufficient* conditions that the constitutive equations satisfy the free-energy imbalance are that[8]

(i) *the free energy determine the stresses* $\mathbf{S}^e$ *and* $\mathbf{S}$ *via the stress relations*

$$\bar{\mathbf{S}}^e(\mathbf{C}^e,\vartheta)=2\,\frac{\partial\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\mathbf{C}^e},\qquad(6.6)$$

$$\bar{\mathbf{S}}(\mathbf{C},\vartheta)=2\,\frac{\partial\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\mathbf{C}},\qquad(6.7)$$

and the components $\eta^{(1)}$, $\eta^{(2)}$, *and* $\eta^{(p)}$ *of the entropy* η_R *via the entropy relations*

$$\bar{\eta}^{(1)}(\mathbf{C}^e,\vartheta)=-\frac{\partial\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\vartheta},$$

$$\bar{\eta}^{(2)}(\mathbf{C},\vartheta)=-\frac{\partial\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\vartheta},\qquad(6.8)$$

$$\bar{\eta}^{(p)}(\mathbf{A},\vartheta)=-\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\vartheta};$$

(ii) *the plastic distortion-rate* $\mathbf{D}^p$ *and the temperature gradient* $\nabla\vartheta$ *satisfy the reduced dissipation inequality*

$$\left(\bar{\mathbf{T}}^p(\mathbf{D}^p,\mathbf{\Lambda})-2\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\right)_0\right):\mathbf{D}^p+\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}:\mathbf{G}(\mathbf{\Lambda})\right)d^p$$

$$+\frac{1}{\vartheta}\,\nabla\vartheta\cdot\mathbf{K}(\vartheta)\nabla\vartheta\geq 0.\qquad(6.9)$$

We assume henceforth that (6.6), (6.7), and (6.8) hold in all motions of the body. We assume further that the material is *strictly dissipative* in the sense that it satisfies the *mechanical dissipation inequality*

$$\mathbf{Y}^p(\mathbf{D}^p,\mathbf{\Lambda}):\mathbf{D}^p+\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}:\mathbf{G}(\mathbf{\Lambda})\right)d^p>0,\qquad(6.10)$$

whenever $\mathbf{D}^p\neq\mathbf{0}$, where we have introduced a *symmetric and deviatoric dissipative flow stress* $\mathbf{Y}^p$ defined by

$$\mathbf{Y}^p(\mathbf{D}^p,\mathbf{\Lambda})\stackrel{\text{def}}{=}\bar{\mathbf{T}}^p(\mathbf{D}^p,\mathbf{\Lambda})-2\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\right)_0;\qquad(6.11)$$

and that the material also separately satisfies the *heat conduction inequality*

$$\frac{1}{\vartheta}\,\nabla\vartheta\cdot\mathbf{K}(\vartheta)\nabla\vartheta>0\quad\text{whenever}\quad\nabla\vartheta\neq\mathbf{0}.\qquad(6.12)$$

The last inequality implies that the thermal conductivity tensor is positive definite.

From (6.11) we note that the stress $\mathbf{T}^p$, which is conjugate to $\mathbf{D}^p$, may be split into a dissipative part and an energetic part as follows:

$$\mathbf{T}^p=\bar{\mathbf{T}}^p(\mathbf{D}^p,\mathbf{\Lambda})=\underbrace{\mathbf{Y}^p(\mathbf{D}^p,\mathbf{\Lambda})}_{\text{dissipative part of }\mathbf{T}^p}+\underbrace{2\left(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\right)_0}_{\text{energetic part of }\mathbf{T}^p}.\qquad(6.13)$$

---

[8]We content ourselves with constitutive equations that are only sufficient, but generally not necessary for compatibility with thermodynamics.

6.2 Further consequences of thermodynamics: Gibbs relations. Entropy relation. Partial differential equation for temperature

In view of (6.1), (6.6), (6.7) and (6.8), we have the *first Gibbs relation*,

$$\dot{\psi}_{\mathrm{R}} = \frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e + \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} - \eta_{\mathrm{R}}\dot{\vartheta} + 2\Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\Big)_0 : \mathbf{D}^p - \Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}} : \mathbf{G}(\mathbf{\Lambda})\Big)d^p, \tag{6.14}$$

which, with (5.4), yields the *second Gibbs relation*

$$\dot{\varepsilon}_{\mathrm{R}} = \vartheta\dot{\eta}_{\mathrm{R}} + \frac{1}{2}\mathbf{S}^e : \dot{\mathbf{C}}^e + \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} + 2\Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}}\mathbf{A}\Big)_0 : \mathbf{D}^p - \Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}} : \mathbf{G}(\mathbf{\Lambda})\Big)d^p. \tag{6.15}$$

Using the second Gibbs relation and (6.11), the balance of energy (5.12) may be written as an *entropy balance*

$$\vartheta\dot{\eta}_{\mathrm{R}} = -\mathrm{Div}\,\mathbf{q}_{\mathrm{R}} + q_{\mathrm{R}} + \mathbf{Y}^p(\mathbf{D}^p,\mathbf{\Lambda}):\mathbf{D}^p + \Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}} : \mathbf{G}(\mathbf{\Lambda})\Big)d^p. \tag{6.16}$$

Granted the thermodynamically restricted constitutive relations (6.6), (6.7) and (6.8), this entropy relation is equivalent to balance of energy.

Next, let

$$\begin{aligned}
\psi_{\mathrm{R}} &= \bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta) + \bar{\psi}^{(2)}(\mathbf{C},\vartheta) + \bar{\psi}^{(p)}(\mathbf{A},\vartheta) \equiv \bar{\psi}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta), \\
\eta_{\mathrm{R}} &= \bar{\eta}^{(1)}(\mathbf{C}^e,\vartheta) + \bar{\eta}^{(2)}(\mathbf{C},\vartheta) + \bar{\eta}^{(p)}(\mathbf{A},\vartheta) \equiv \bar{\eta}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta),
\end{aligned} \tag{6.17}$$

then the internal energy density is given by

$$\varepsilon_{\mathrm{R}} = \bar{\varepsilon}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta) \overset{\mathrm{def}}{=} \bar{\psi}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta) + \vartheta\bar{\eta}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta), \tag{6.18}$$

and, as is standard, the *specific heat* is defined by

$$c \overset{\mathrm{def}}{=} \frac{\partial\bar{\varepsilon}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta)}{\partial\vartheta}. \tag{6.19}$$

Hence, from (6.18)

$$c \overset{\mathrm{def}}{=} \Big(\frac{\partial\bar{\psi}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta)}{\partial\vartheta} + \bar{\eta}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta) + \vartheta\frac{\partial\bar{\eta}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta)}{\partial\vartheta}\Big), \tag{6.20}$$

and use of (6.8) and (6.17) gives

$$c \overset{\mathrm{def}}{=} -\vartheta\frac{\partial^2\bar{\psi}(\mathbf{C}^e,\mathbf{C},\mathbf{A},\vartheta)}{\partial\vartheta^2} = -\vartheta\Big(\frac{\partial^2\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\vartheta^2} + \frac{\partial^2\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\vartheta^2} + \frac{\partial^2\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\vartheta^2}\Big). \tag{6.21}$$

Next, from (6.8) and (6.21)

$$\vartheta\,\dot{\eta}_r = -\vartheta\frac{\partial^2\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\vartheta\,\partial\mathbf{C}^e}:\dot{\mathbf{C}}^e - \vartheta\frac{\partial^2\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\vartheta\,\partial\mathbf{C}}:\dot{\mathbf{C}} - \vartheta\frac{\partial^2\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\vartheta\,\partial\mathbf{A}}:\dot{\mathbf{A}} + c\,\dot{\vartheta}. \tag{6.22}$$

Then, using (6.21) and (6.22) in (6.16) gives the following partial differential equation for the temperature

$$\begin{aligned}
c\dot{\vartheta} = &-\mathrm{Div}\,\mathbf{q}_{\mathrm{R}} + q_{\mathrm{R}} + \mathbf{Y}^p(\mathbf{D}^p,\mathbf{\Lambda}):\mathbf{D}^p + \Big(\frac{\partial\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\mathbf{A}} : \mathbf{G}(\mathbf{\Lambda})\Big)d^p \\
&+ \vartheta\frac{\partial^2\bar{\psi}^{(1)}(\mathbf{C}^e,\vartheta)}{\partial\vartheta\,\partial\mathbf{C}^e}:\dot{\mathbf{C}}^e + \vartheta\frac{\partial^2\bar{\psi}^{(2)}(\mathbf{C},\vartheta)}{\partial\vartheta\,\partial\mathbf{C}}:\dot{\mathbf{C}} + \vartheta\frac{\partial^2\bar{\psi}^{(p)}(\mathbf{A},\vartheta)}{\partial\vartheta\,\partial\mathbf{A}}:\dot{\mathbf{A}}.
\end{aligned} \tag{6.23}$$

6.3 Isotropy

The following definitions help to make precise our notion of an isotropic material (cf., Anand and Gurtin, 2003):

(i) Orth^{+} = the group of all rotations (the proper orthogonal group);

(ii) the *symmetry group* $\mathcal{G}_{\mathrm{R}}$, is the group of all rotations of the *reference* configuration that leaves the response of the material unaltered;

(ii) the *symmetry group* $\mathcal{G}_{\mathrm{I}}$ at each time t, is the group of all rotations of the *intermediate* structural space that leaves the response of the material unaltered.

We now discuss the manner in which the basic fields transform under such transformations, granted the physically natural requirement of invariance of the internal power (5.11), or equivalently, the requirement that

$$\mathbf{S}^{e}\!:\!\dot{\mathbf{C}}^{e}, \quad \mathbf{S}\!:\!\dot{\mathbf{C}}, \quad \text{and} \quad \mathbf{T}^{p}\!:\!\mathbf{D}^{p} \quad \text{be invariant.} \tag{6.24}$$

6.3.1 Isotropy of the reference space

Let $\mathbf{Q}$ be a *time-independent rotation of the reference configuration*. Then $\mathbf{F} \to \mathbf{FQ}$, and hence

$$\mathbf{C} \to \mathbf{Q}^{\top}\mathbf{CQ}, \quad \mathbf{F}^{p} \to \mathbf{F}^{p}\mathbf{Q}, \quad \text{and} \quad \mathbf{F}^{e} \text{ is invariant, and hence } \mathbf{C}^{e} \text{ and } \mathbf{B}^{p} \text{ are invariant,} \tag{6.25}$$

so that, by (2.5) and (2.12),

$$\dot{\mathbf{C}} \to \mathbf{Q}^{\top}\dot{\mathbf{C}}\mathbf{Q}, \quad \text{while } \dot{\mathbf{C}}^{e} \text{ and } \mathbf{D}^{p} \text{ are invariant.}$$

We may therefore use (6.24) to conclude that

$$\mathbf{S} \to \mathbf{Q}^{\top}\mathbf{SQ}, \quad \text{while } \mathbf{S}^{e} \text{ and } \mathbf{T}^{p} \text{ are invariant.} \tag{6.26}$$

Further, since the tensor $\mathbf{A}$ maps vectors in the intermediate space into vectors in the same space, $\mathbf{A}$ is invariant, and since $\boldsymbol{\xi}$ are scalars, they too are invariant. Thus, with reference to (6.1), the constitutive functions $\bar{\psi}^{(2)}$, $\bar{\eta}^{(2)}$, and $\bar{\mathbf{S}}$ must satisfy

$$\left. \begin{array}{l} \bar{\psi}^{(2)}(\mathbf{C},\vartheta) = \bar{\psi}^{(2)}(\mathbf{Q}^{\top}\mathbf{CQ},\vartheta), \\[2mm] \bar{\eta}^{(2)}(\mathbf{C},\vartheta) = \bar{\eta}^{(2)}(\mathbf{Q}^{\top}\mathbf{CQ},\vartheta), \\[2mm] \mathbf{Q}^{\top}\bar{\mathbf{S}}(\mathbf{C},\vartheta)\mathbf{Q} = \bar{\mathbf{S}}(\mathbf{Q}^{\top}\mathbf{CQ},\vartheta), \end{array} \right\} \tag{6.27}$$

for all symmetric positive definite tensors $\mathbf{C}$, and all rotations $\mathbf{Q} \in \mathcal{G}_{\mathrm{R}}$.

Turning our attention next to the constitutive equation (6.3) for the heat flux, a standard result from the theory of finite thermoelasticity is that under a symmetry transformation $\mathbf{Q}$ for the reference configuration, the temperature gradient $\nabla\vartheta$ and the heat flux $\mathbf{q}_{\mathrm{R}}$ transform as

$$\nabla\vartheta \to \mathbf{Q}^{\top}\nabla\vartheta, \qquad \mathbf{q}_{\mathrm{R}} \to \mathbf{Q}^{\top}\mathbf{q}_{\mathrm{R}}.$$

Hence, from (6.3) the thermal conductivity tensor must obey

$$\mathbf{K}(\vartheta) = \mathbf{Q}^{\top}\mathbf{K}(\vartheta)\mathbf{Q} \tag{6.28}$$

for all rotations $\mathbf{Q}$ in the symmetry group $\mathcal{G}_{\mathrm{R}}$.

We refer to the material as *initially isotropic* (and to the reference configuration as undistorted) if

$$\mathcal{G}_{\mathrm{R}} = \mathrm{Orth}^{+} \tag{6.29}$$

so that the response of the material is invariant under arbitrary rotations of the reference space. Henceforth

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- *we restrict attention to materials that are initially isotropic.*

In this case,

(†) the response functions $\bar{\psi}^{(2)}$, $\bar{\eta}^{(2)}$, and $\bar{\mathbf{S}}$, must each be *isotropic*,

and that the thermal conductivity has the representation

$$\mathbf{K}(\vartheta) = \kappa(\vartheta)\mathbf{1}, \qquad \text{with} \qquad \kappa(\vartheta) > 0 \tag{6.30}$$

a scalar thermal conductivity.

6.3.2 Isotropy of the intermediate structural space

Next, let $\mathbf{Q}$, a *time-independent rotation of the intermediate space*, be a symmetry transformation. Then $\mathbf{F}$ is unaltered by such a rotation, and hence

$$\mathbf{F}^e \to \mathbf{F}^e\mathbf{Q} \quad \text{and} \quad \mathbf{F}^p \to \mathbf{Q}^\top\mathbf{F}^p, \tag{6.31}$$

and also

$$\mathbf{C}^e \to \mathbf{Q}^\top\mathbf{C}^e\mathbf{Q}, \qquad \mathbf{B}^p \to \mathbf{Q}^\top\mathbf{B}^p\mathbf{Q}, \qquad \dot{\mathbf{C}}^e \to \mathbf{Q}^\top\dot{\mathbf{C}}^e\mathbf{Q}, \qquad \mathbf{D}^p \to \mathbf{Q}^\top\mathbf{D}^p\mathbf{Q}. \tag{6.32}$$

Further, since the tensor $\mathbf{A}$ maps vectors in the intermediate space into vectors in the same space, we assume that $\mathbf{A}$ transforms as

$$\mathbf{A} \to \mathbf{Q}^\top\mathbf{A}\mathbf{Q},$$

and hence

$$\dot{\mathbf{A}} \to \mathbf{Q}^\top\dot{\mathbf{A}}\mathbf{Q}.$$

Then (6.32) and (6.24) yield the transformation laws

$$\mathbf{S}^e \to \mathbf{Q}^\top\mathbf{S}^e\mathbf{Q}, \qquad \mathbf{T}^p \to \mathbf{Q}^\top\mathbf{T}^p\mathbf{Q}. \tag{6.33}$$

Thus, with reference to the constitutive equations (6.1) we conclude that

$$\left.\begin{aligned}
\bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta) &= \bar{\psi}^{(1)}(\mathbf{Q}^\top\mathbf{C}^e\mathbf{Q}, \vartheta), \qquad \bar{\psi}^{(p)}(\mathbf{A}, \vartheta) = \bar{\psi}^{(p)}(\mathbf{Q}^\top\mathbf{A}\mathbf{Q}, \vartheta), \\
\bar{\eta}^{(1)}(\mathbf{C}^e, \vartheta) &= \bar{\eta}^{(1)}(\mathbf{Q}^\top\mathbf{C}^e\mathbf{Q}, \vartheta), \qquad \bar{\eta}^{(p)}(\mathbf{A}, \vartheta) = \bar{\eta}^{(p)}(\mathbf{Q}^\top\mathbf{A}\mathbf{Q}, \vartheta), \\
\mathbf{Q}^\top\bar{\mathbf{S}}^e(\mathbf{C}^e, \vartheta)\mathbf{Q} &= \bar{\mathbf{S}}^e(\mathbf{Q}^\top\mathbf{C}^e\mathbf{Q}, \vartheta), \\
\mathbf{Q}^\top\bar{\mathbf{T}}^p(\mathbf{D}^p, \boldsymbol{\Lambda})\mathbf{Q} &= \bar{\mathbf{T}}^p(\mathbf{Q}^\top\mathbf{D}^p\mathbf{Q}, \mathbf{Q}^\top\boldsymbol{\Lambda}\mathbf{Q}), \\
h_i(\mathbf{D}^p, \boldsymbol{\Lambda}) &= h_i(\mathbf{Q}^\top\mathbf{D}^p\mathbf{Q}, \mathbf{Q}^\top\boldsymbol{\Lambda}\mathbf{Q}), \\
\mathbf{Q}^\top\mathbf{G}(\mathbf{D}^p, \boldsymbol{\Lambda})\mathbf{Q} &= \mathbf{G}(\mathbf{Q}^\top\mathbf{D}^p\mathbf{Q}, \mathbf{Q}^\top\boldsymbol{\Lambda}\mathbf{Q}),
\end{aligned}\right\} \tag{6.34}$$

with

$$\mathbf{Q}^\top\boldsymbol{\Lambda}\mathbf{Q} = (\mathbf{Q}^\top\mathbf{C}^e\mathbf{Q}, \mathbf{Q}^\top\mathbf{B}^p\mathbf{Q}, \mathbf{Q}^\top\mathbf{A}\mathbf{Q}, \boldsymbol{\xi}, \vartheta),$$

must hold for all rotations $\mathbf{Q}$ in the *symmetry group* $\mathcal{G}_\mathrm{I}$ at each time t.

We refer to the material as one which is *continually isotropic*, if in addition to the referential isotropy discussed in the previous subsection,

$$\mathcal{G}_\mathrm{I} = \mathrm{Orth}^+, \tag{6.35}$$

so that the response of the material is also invariant under arbitrary rotations of the intermediate space at each time t. Henceforth

- *we restrict attention to materials that are not only initially, but also continually isotropic.*

In this case, in addition to the requirements (†) on $\bar{\psi}^{(2)}$, $\bar{\eta}^{(2)}$, and $\bar{\mathbf{S}}$ from isotropy of the reference space,

(‡) the response functions $\bar{\psi}^{(1)}$, $\bar{\psi}^{(p)}$, $\bar{\eta}^{(1)}$, $\bar{\eta}^{(p)}$, $\bar{\mathbf{S}}^e$, $\bar{\mathbf{T}}^p$, h_i, and $\mathbf{G}$ must also each be *isotropic*.

6.4 Consequences of isotropy of the free energy

Since $\bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta)$ is an isotropic function of $\mathbf{C}^e$, it has the representation

$$\bar{\psi}^{(1)}(\mathbf{C}^e, \vartheta) = \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta), \tag{6.36}$$

where

$$\mathcal{I}_{\mathbf{C}^e} = \Big(I_1(\mathbf{C}^e), I_2(\mathbf{C}^e), I_3(\mathbf{C}^e) \Big)$$

is the list of principal invariants of $\mathbf{C}^e$. Thus, from (6.6),

$$\mathbf{S}^e = \bar{\mathbf{S}}^e(\mathbf{C}^e, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta)}{\partial \mathbf{C}^e}, \tag{6.37}$$

and that $\bar{\mathbf{S}}^e(\mathbf{C}^e, \vartheta)$ is an *isotropic function of* $\mathbf{C}^e$. Then since the Mandel stress is defined by (cf. (5.8))

$$\mathbf{M}^e = \mathbf{C}^e \mathbf{S}^e,$$

and $\bar{\mathbf{S}}^e(\mathbf{C}^e, \vartheta)$ is isotropic, we find that $\mathbf{S}^e$ and $\mathbf{C}^e$ commute,

$$\mathbf{C}^e \mathbf{S}^e = \mathbf{S}^e \mathbf{C}^e, \tag{6.38}$$

and hence that *the Mandel stress* $\mathbf{M}^e$ *is symmetric.*

Similarly, since $\bar{\psi}^{(2)}(\mathbf{C}, \vartheta)$ is an isotropic function of $\mathbf{C}$, it has the representation

$$\bar{\psi}^{(2)}(\mathbf{C}, \vartheta) = \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta), \quad \text{where} \quad \mathcal{I}_{\mathbf{C}} = \Big(I_1(\mathbf{C}), I_2(\mathbf{C}), I_3(\mathbf{C}) \Big), \tag{6.39}$$

and from (6.7),

$$\mathbf{S} = \bar{\mathbf{S}}(\mathbf{C}, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta)}{\partial \mathbf{C}}. \tag{6.40}$$

Further the defect free energy has a representation

$$\bar{\psi}^{(p)} = \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta) \quad \text{where} \quad \mathcal{I}_{\mathbf{A}} = \Big(I_1(\mathbf{A}), I_2(\mathbf{A}), I_3(\mathbf{A}) \Big), \tag{6.41}$$

and this yields that

$$\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}} \mathbf{A}, \tag{6.42}$$

is a *symmetric* tensor.

7 Flow rule

Recall from (6.13) that the constitutive equation for $\mathbf{T}^p$ is

$$\mathbf{T}^p = \underbrace{2 \left(\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}} \mathbf{A} \right)_0}_{\text{energetic part of } \mathbf{T}^p} + \underbrace{\mathbf{Y}^p(\mathbf{D}^p, \mathbf{\Lambda})}_{\text{dissipative part of } \mathbf{T}^p}. \tag{7.1}$$

We denote the energetic part of $\mathbf{T}^p$ by

$$\mathbf{M}_{\text{back}} \overset{\text{def}}{=} 2 \left(\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}} \mathbf{A} \right)_0, \tag{7.2}$$

and call it a *back-stress*, and denote an *effective Mandel stress* by

$$\mathbf{M}_{\text{eff}}^e \overset{\text{def}}{=} \mathbf{M}^e - \mathbf{M}_{\text{back}}. \tag{7.3}$$

Then, upon using the constitutive relation (7.1) and the microforce balance (4.28), together with symmetry of the Mandel stress discussed above, a central result of the theory is the *flow rule*

$$(\mathbf{M}_{\text{eff}}^e)_0 = \mathbf{Y}^p(\mathbf{D}^p, \mathbf{\Lambda}). \tag{7.4}$$

We now make two major assumptions concerning the plastic flow for isotropic materials:

(1) Let

$$\mathbf{N}^p \overset{\text{def}}{=} \frac{\mathbf{D}^p}{d^p} \tag{7.5}$$

denote the *direction of plastic flow* whenever $\mathbf{D}^p \neq \mathbf{0}$, then the mechanical dissipation inequality (6.10) may be written as

$$\left(\mathbf{Y}^p(d^p, \mathbf{N}^p, \boldsymbol{\Lambda}) : \mathbf{N}^p + \left(\frac{\partial \bar{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \mathbf{G}(\boldsymbol{\Lambda}) \right) \right) d^p > 0 \quad \text{when} \quad \mathbf{D}^p \neq \mathbf{0}. \tag{7.6}$$

Guided by (7.6), we assume henceforth that the dissipative flow stress $\mathbf{Y}^p$ is parallel to and points in the same direction as $\mathbf{N}^p$, so that[9]

$$\mathbf{Y}^p(d^p, \mathbf{N}^p, \boldsymbol{\Lambda}) = Y(d^p, \mathbf{N}^p, \boldsymbol{\Lambda})\mathbf{N}^p, \tag{7.7}$$

where

$$Y(d^p, \mathbf{N}^p, \boldsymbol{\Lambda}) = \mathbf{Y}^p(d^p, \mathbf{N}^p, \boldsymbol{\Lambda}) : \mathbf{N}^p \tag{7.8}$$

represents a scalar *flow strength* of the material.

(2) We also assume that the scalar flow strength $Y(d^p, \mathbf{N}^p, \boldsymbol{\Lambda})$ and the function $h_i(d^p, \mathbf{N}^p, \boldsymbol{\Lambda})$ characterizing the evolution of the scalar internal variable ξ_i are independent of the flow direction $\mathbf{N}^p$, so that

$$Y(d^p, \boldsymbol{\Lambda}), \qquad h_i(d^p, \boldsymbol{\Lambda}). \tag{7.9}$$

Thus, using $(7.9)_1$ and (7.7), the flow rule (7.4) reduces to,

$$(\mathbf{M}_{\text{eff}}^e)_0 = Y(d^p, \boldsymbol{\Lambda})\mathbf{N}^p \tag{7.10}$$

which immediately gives

$$\mathbf{N}^p = \frac{(\mathbf{M}_{\text{eff}}^e)_0}{|(\mathbf{M}_{\text{eff}}^e)_0|}, \tag{7.11}$$

and

$$|(\mathbf{M}_{\text{eff}}^e)_0| = Y(d^p, \boldsymbol{\Lambda}). \tag{7.12}$$

When $|(\mathbf{M}_{\text{eff}}^e)_0|$ and $\boldsymbol{\Lambda}$ are known, (7.12) serves as an implicit equation for the scalar flow rate d^p.

Finally, using (7.8), $(7.9)_1$ and (7.12), the mechanical dissipation inequality (7.6) reduces to

$$\left(|(\mathbf{M}_{\text{eff}}^e)_0| + \left(\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}} : \mathbf{G}(\boldsymbol{\Lambda}) \right) \right) d^p > 0 \qquad \text{when} \quad d^p \neq 0. \tag{7.13}$$

8 Summary

In this section we summarize our theory for isotropic elastic viscoplastic materials intended (when further specialized) for application to amorphous polymeric materials. The theory relates the following basic fields:

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[9]This assumption corresponds to the classical notion of *maximal dissipation* in Mises-type theories of metal plasticity.

$$\begin{aligned}
&\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t), && \text{motion;} \\
&\mathbf{F} = \nabla\boldsymbol{\chi}, \quad J = \det \mathbf{F} > 0, && \text{deformation gradient;} \\
&\mathbf{F} = \mathbf{F}^e \mathbf{F}^p, && \text{elastic-plastic decomposition of } \mathbf{F}; \\
&\mathbf{F}^e, \quad J^e = \det \mathbf{F}^e = J > 0, && \text{elastic distortion;} \\
&\mathbf{F}^p, \quad J^p = \det \mathbf{F}^p = 1, && \text{inelastic distortion;} \\
&\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e, && \text{polar decomposition of } \mathbf{F}^e; \\
&\mathbf{C} = \mathbf{F}^\top \mathbf{F}, && \text{right Cauchy-Green tensor;} \\
&\mathbf{C}^e = \mathbf{F}^{e\top} \mathbf{F}^e,, && \text{elastic right Cauchy-Green tensors;} \\
&\mathbf{B}^p = \mathbf{F}^p \mathbf{F}^{p\top}, && \text{plastic left Cauchy-Green tensor;} \\
&\mathbf{T} = \mathbf{T}^\top, && \text{Cauchy stress;} \\
&\mathbf{T}_{\mathrm{R}} = J \mathbf{T} \mathbf{F}^{-\top}, && \text{Piola stress;} \\
&\psi_{\mathrm{R}}, && \text{free energy density per unit reference volume;} \\
&\eta_{\mathrm{R}}, && \text{entropy density per unit reference volume;} \\
&\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_m) && m \text{ scalar internal variables;} \\
&\mathbf{A}, \quad \mathbf{A} = \mathbf{A}^\top, \quad \det \mathbf{A} = 1 && \text{tensorial internal variable;} \\
&\vartheta > 0, && \text{absolute temperature;} \\
&\nabla\vartheta, && \text{referential temperature gradient;} \\
&\mathbf{q}_{\mathrm{R}}, && \text{referential heat flux vector.}
\end{aligned}$$

8.1 Constitutive equations

1. **Free energy**

$$\psi_{\mathrm{R}} = \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta) + \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta) + \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta), \tag{8.1}$$

where $\mathcal{I}_{\mathbf{C}^e}$, $\mathcal{I}_{\mathbf{A}}$, and $\mathcal{I}_{\mathbf{C}}$ are the lists of the principal invariants of $\mathbf{C}^e$, $\mathbf{C}$, and $\mathbf{A}$, respectively.

2. **Cauchy stress**

$$\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)}, \tag{8.2}$$

with

$$\mathbf{T}^{(1)} \stackrel{\text{def}}{=} J^{-1}\left(\mathbf{F}^e \mathbf{S}^e \mathbf{F}^{e\top}\right), \qquad \mathbf{S}^e = 2\frac{\partial \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta)}{\partial \mathbf{C}^e}, \tag{8.3}$$

and

$$\mathbf{T}^{(2)} \stackrel{\text{def}}{=} J^{-1}\left(\mathbf{F}\mathbf{S}\mathbf{F}^\top\right), \qquad \mathbf{S} = 2\frac{\partial \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta)}{\partial \mathbf{C}}. \tag{8.4}$$

3. **Driving stresses for plastic flow**

With

$$\mathbf{M}^e = \mathbf{C}^e \mathbf{S}^e, \tag{8.5}$$

denoting the *symmetric* Mandel stress,

$$\mathbf{M}_{\mathrm{back}} = 2\left(\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}}\mathbf{A}\right)_0, \tag{8.6}$$

a *symmetric deviatoric* back-stress, and

$$\mathbf{M}_{\mathrm{eff}}^e = \mathbf{M}^e - \mathbf{M}_{\mathrm{back}} \tag{8.7}$$

an *effective Mandel stress*. The driving stress for plastic flow is taken as the stress difference

$$(\mathbf{M}_{\mathrm{eff}}^e)_0 = \mathbf{M}_0^e - \mathbf{M}_{\mathrm{back}}, \tag{8.8}$$

which is the symmetric and deviatoric.

4. **Flow rule**

The evolution equation for $\mathbf{F}^p$ is

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \, \mathbf{F}^p, \tag{8.9}$$

with $\mathbf{D}^p$ given by

$$\mathbf{D}^p = d^p \, \mathbf{N}^p, \qquad \mathbf{N}^p = \frac{(\mathbf{M}^e_{\mathrm{eff}})_0}{|(\mathbf{M}^e_{\mathrm{eff}})_0|}, \tag{8.10}$$

where with

$$\mathbf{\Lambda} \overset{\mathrm{def}}{=} \{\mathbf{C}^e, \mathbf{B}^p, \mathbf{A}, \boldsymbol{\xi}, \vartheta\}, \tag{8.11}$$

the scalar flow rate d^p is obtained by solving the scalar strength relation

$$|(\mathbf{M}^e_{\mathrm{eff}})_0| = Y(d^p, \mathbf{\Lambda}), \tag{8.12}$$

for given $(\mathbf{M}^e_{\mathrm{eff}})_0$ and $\mathbf{\Lambda}$, where the strength function $Y(d^p, \mathbf{\Lambda})$ is an isotropic function of its arguments.

5. **Evolution equations for internal variables**

$$\left.\begin{aligned}
\dot{\xi}_i &= h_i(d^p, \mathbf{\Lambda}), \\
\dot{\mathbf{A}} &= \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\mathbf{\Lambda}) d^p,
\end{aligned}\right\} \tag{8.13}$$

with the functions h_i and $\mathbf{G}$ isotropic functions of their arguments. Further, the recovery function $\mathbf{G}(\mathbf{\Lambda})$ is constrained to satisfy $\mathrm{tr}\,(\mathbf{G}(\mathbf{\Lambda})\mathbf{A}^{-1}) = 0$.

The evolution equations for $\mathbf{F}^p$, $\boldsymbol{\xi}$ and $\mathbf{A}$ need to be accompanied by initial conditions. Typical initial conditions presume that the body is initially (at time $t = 0$, say) in a **virgin state** in the sense that

$$\mathbf{F}(\mathbf{X}, 0) = \mathbf{F}^p(\mathbf{X}, 0) = \mathbf{A}(\mathbf{X}, 0) = \mathbf{1}, \qquad \xi_i(\mathbf{X}, 0) = \xi_{i,0} \; (= \text{constant}), \tag{8.14}$$

so that by $\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$ we also have $\mathbf{F}^e(\mathbf{X}, 0) = \mathbf{1}$.

6. **Entropy relation. Fourier's Law**

Finally, we have the entropy relation

$$\eta_{\mathrm{R}} = -\left(\frac{\partial \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta)}{\partial \vartheta} + \frac{\partial \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta)}{\partial \vartheta} + \frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \vartheta}\right), \tag{8.15}$$

together with Fourier's law

$$\mathbf{q}_{\mathrm{R}} = -\kappa \, \nabla \vartheta, \tag{8.16}$$

with $\kappa(\vartheta) > 0$ the thermal conductivity.

8.2 Partial differential equations for the deformation and temperature fields

The partial differential equation for the deformation is obtained from the local force balance (cf. (4.19)),

$$\mathrm{Div}\,\mathbf{T}_{\mathrm{R}} + \mathbf{b}_{0\mathrm{R}} = \rho_{\mathrm{R}} \, \ddot{\boldsymbol{\chi}}, \tag{8.17}$$

where $\mathbf{b}_{0\mathrm{R}}$ is the non-inertial body force, ρ_{R} is the mass density in the reference body, and $\ddot{\boldsymbol{\chi}}$ is the acceleration.

The specific heat in the theory is given by

$$c \overset{\mathrm{def}}{=} -\vartheta \left(\frac{\partial^2 \tilde{\psi}^{(1)}(\mathcal{I}_{\mathbf{C}^e}, \vartheta)}{\partial \vartheta^2} + \frac{\partial^2 \tilde{\psi}^{(2)}(\mathcal{I}_{\mathbf{C}}, \vartheta)}{\partial \vartheta^2} + \frac{\partial^2 \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \vartheta^2}\right), \tag{8.18}$$

and balance of energy, cf. (6.23), together with (7.13), (8.3) and (8.4) gives the following partial differential equation for the temperature

$$
\begin{aligned}
c\dot{\vartheta} = &-\mathrm{Div}\,\mathbf{q}_{\mathrm{R}} + q_{\mathrm{R}} + \left(|(\mathbf{M}^e_{\mathrm{eff}})_0| + \left(\frac{\partial \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \mathbf{A}} : \mathbf{G}(\mathbf{\Lambda})\right)\right) d^p \\
&+ \tfrac{1}{2}\vartheta \, \frac{\partial \mathbf{S}^e}{\partial \vartheta} : \dot{\mathbf{C}}^e + \tfrac{1}{2}\vartheta \, \frac{\partial \mathbf{S}}{\partial \vartheta} : \dot{\mathbf{C}} + \vartheta \, \frac{\partial^2 \tilde{\psi}^{(p)}(\mathcal{I}_{\mathbf{A}}, \vartheta)}{\partial \vartheta \, \partial \mathbf{A}} : \dot{\mathbf{A}}.
\end{aligned}
\tag{8.19}
$$

9   Concluding Remarks

In a companion paper, Part II, we report on a set of recently performed experiments on three important amorphous polymers. There, based on our experiments and based on experience with other existing recent theories of isotropic viscoplasticity of polymeric materials, we further specialize the constitutive theory developed here by imposing additional constitutive assumptions, and calibrate the material parameters appearing in the theory to reproduce the experimentally-measured stress-strain curves for the three amorphous polymeric materials under study. The specialized theory has been numerically implemented in a finite element program, and experimental validation studies to check the predictive capabilities of the constitutive model and computational procedures are also reported in the companion paper.

References

Anand, L., and Gurtin, M.E., 2003. A theory of amorphous solids undergoing large deformations, with applications to polymeric glasses, *International Journal of Solids and Structures* **40**, 1465-1487.

Anand, L., and Ames, N. M., 2006. On modeling the micro-indentation response of an amorphous polymer. *International Journal of Plasticity* **22**, 1123-1170.

Armstrong, P. J., and Frederick, C. O., 1966. A mathematical representation of the multiaxial Bauschinger effect. Report RD/B/N731, CEGB, Central Electricity Generating Board, Berkeley, UK.

Arruda, E. M., and Boyce, M.C., 1993. Evolution of plastic anisotropy in amorphous polymers during finite straining. *International Journal of Plasticity* **9**, 697-720.

Arruda, E.M., Boyce, M.C., Jayachandran, R., 1995. Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers. Mechanics of Materials **19**, 193-212.

Bauschinger, J., 1886. Über die Veränderung der Position der Elastizitätsgrenze des Eisens und Stahls durch Strecken und Quetschen und durch Erwärmen und Abkühlen und durch oftmals wiederholte Beanspruchungen. *Mitteilung aus dem Mechanisch-technischen Laboratorium der Königlichen polytechnischen Hochschule in München* **13**, 1–115.

Basu, S., and Van der Giessen, E., 2002. A thermo-mechanical study of mode I, small-scale yielding crack-tip fields in glassy polymers. *International Journal of Plasticity* **18**, 13951423.

Bergström, J. S., and Boyce, M. C., 1998. Constitutive modeling of large strain time-depedendent behavior of elastomers. *Journal of the Mechanics and Physics of Solids* **46**, 931-954.

Bergström J. S., and Boyce, M. C., 2001. Constitutive modeling of the time-dependent and cyclic loading of elastomers and application to soft biological tissues. *Mechanics of Materials* **33**, 523-530.

Boyce, M.C., Parks, D.M., and Argon, A. S., 1988. Large inelastic deformation of glassy polymers. Part 1: rate dependent constitutive model. *Mechanics of Materials* **7**, 15-33.

Chaboche, J. L., 2008. A review of some plasticity and viscoplasticity constitutive theories. *International Journal of Plasticity.* doi: 10.1016/j.ijplas.2008.03.009

Estevez, R., Basu, S., and Van der Giessen, E., 2005. Analysis of temperature effects near mode I cracks in glassy polymers. *International Journal of Fracture* **132** 249-273.

Estevez, R., and Basu, S., 2008. On the importance of thermo-elastic cooling in the fracture of glassy polymers at high rates. *International Journal of Solids and Structures* **45** 3449-3465.

Govaert, L. E., Timmermans, P. H. M., and Brekelmans, W. A. M, 2000. The influence of intrinsic strain softening on strain localization in polycarbonate: modeling and experimental validation, *Journal of Engineering Materials and Technology* **122**, 177-185.

Gurtin, M. E., 2000. On the plasticity of single crystals: free energy, microscopic forces, plastic strain gradients. *Journal of the Mechanics and Physics of Solids* **48**, 989-1036.

Gurtin, M.E., and Anand, L., 2005. The decomposition $\mathbf{F} = \mathbf{F}^e\mathbf{F}^p$, material symmetry, and plastic irrotationality for solids that are isotropic-viscoplastic or amorphous. *International Journal of Plasticity* **21**, 1686-1719.

Hasan, O. A., and Boyce, M. C., 1995. A constitutive model for the nonlinear viscoelastic viscoplastic behavior of glassy polymers. *Polymer Engineering and Science* **35**, 331-344.

Haward, R. N. and Thackray, G., 1968. The use of a mathematical model to describe isothermal stress-strain curves in glassy polymers. *Proceedings of the Royal Society, London A* **302**, 453-472.

Haward, R. N., and Young, R. J., 1997. The Physics of Glassy Polymers 2nd Ed. Chapman & Hall, London.

Haupt, P., and Sedlan, K., 2001. Viscoplasticity of elastomeric materials. Experimental facts and constitutive modelling. *Archive of Applied Mechanics* **71**, 89–109.

Henann, D., and Anand, L., 2008. A large deformation theory for rate-dependent elastic-plastic materials with combined isotropic and kinematic hardening. *International Journal of Plasticity*, submitted.

Kröner, E., 1960. Allgemeine kontinuumstheorie der versetzungen und eigenspannungen. *Archive for Rational Mechanics and Analysis* **4**, 273-334.

Lee, E. H., 1969. Elastic plastic deformation at finite strain. *ASME Journal of Applied Mechanics* **36**, 1-6.

Lion, A., 1997. On the large deformation behaviour of reinforced rubber at different temperatures. *Journal of the Mechanics and Physics of Solids* **45**, 1805–1834.

Lion, A., 2000. Consitutive modeling in finite thermoviscoplasticity: a physical approach based on nonlinear rheological models. *International Journal of Plasticity* **16**, 469–494.

Parks, D. M., Argon, A. S., and Bagepalli, B., 1985. Large elastic-plastic deformation of glassy polymers, part 1: Constitutive modelling. Report, MIT, Program in Polymer Science and Technology.

Reese, S., and Govindjee, S., 1998. A theory of finite viscoelasticity and numerical aspects. *International Journal of Solids and Structures* **35**, 3455-3482.

Truesdell, C., and Noll, W., 1965. *The Nonlinear Field Theories of Mechanics*. In Flügge, S. (Ed.), *Handbuch der Physik* III/3. Springer, Berlin.

Wu, P. D. and Van der Giessen, E., 1993. On improved network models for rubber elasticity and their applications to orientation hardening of glassy polymers. *Journal of the Mechanics and Physics of Solids* **41**, 427-456.