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

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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)

\[
\mathbf{F} = \mathbf{F}^e \mathbf{F}^p
\] (1.1)

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of the deformation gradient $F$ into elastic and plastic parts $F^e$ and $F^p$ (e.g., Boyce et al., 1988, Arruda and Boyce, 1993; Wu and Van der Giesen, 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 $F^p$ through $B^p = F^p F^{p\top}$, 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 $F$ through $C = F^{\top} F$.

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). 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

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

which represents a dimensionless squared stretch-like quantity, and assumed that the free energy density $\psi_R$ is given by

$$\psi_R = \tilde{\psi}^{(1)}(C^e, \vartheta) + \tilde{\psi}^{(2)}(C, \vartheta) + \tilde{\psi}^{(p)}(A, \vartheta),$$

where $\vartheta$ is the absolute temperature. Here, $\tilde{\psi}^{(1)}$ is an energy associated with intermolecular interactions and modeled using the elastic Cauchy-Green tensor $C^e = F^{e\top} F^e$, $\tilde{\psi}^{(2)}$ an energy associated with the stretching of the polymer chains and modeled (as discussed above) using the total Cauchy-Green tensor $C = F^{\top} F$, and $\tilde{\psi}^{(p)}$ a “defect-energy” associated with plastic deformation and introduced via the internal variable $A$. 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 $X$ an arbitrary material point of $B$. A motion of $B$ is then a smooth one-to-one
mapping \( \mathbf{x} = \mathbf{\chi}(\mathbf{X}, t) \) with deformation gradient, velocity, and velocity gradient given by\(^2\)

\[
\mathbf{F} = \nabla \mathbf{\chi}, \quad \mathbf{v} = \dot{\mathbf{\chi}}, \quad \mathbf{L} = \text{grad} \mathbf{v} = \dot{\mathbf{F}} \mathbf{F}^{-1}.
\]

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)

\[
\mathbf{F} = \mathbf{F}^e \mathbf{F}^p.
\]

As is standard, we assume that

\[
J = \det \mathbf{F} > 0,
\]

and consistent with this we assume that

\[
J^e \overset{\text{def}}{=} \det \mathbf{F}^e > 0, \quad J^p \overset{\text{def}}{=} \det \mathbf{F}^p > 0,
\]

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),

\[
\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1},
\]

with

\[
\mathbf{L}^e = \dot{\mathbf{F}}^e \mathbf{F}^{e-1}, \quad \mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1}.
\]

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

\[
\mathbf{D} = \text{sym} \mathbf{L}, \quad \mathbf{W} = \text{skw} \mathbf{L},
\]

\[
\begin{align*}
\mathbf{D}^e &= \text{sym} \mathbf{L}^e, \quad \mathbf{W}^e = \text{skw} \mathbf{L}^e, \\
\mathbf{D}^p &= \text{sym} \mathbf{L}^p, \quad \mathbf{W}^p = \text{skw} \mathbf{L}^p,
\end{align*}
\]

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

\[
\mathbf{F} = \mathbf{R} \mathbf{U} = \mathbf{V} \mathbf{R},
\]

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

\[
\mathbf{U} = \sqrt{\mathbf{F}^\top \mathbf{F}}, \quad \mathbf{V} = \sqrt{\mathbf{F} \mathbf{F}^\top}.
\]

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

\[
\mathbf{C} = \mathbf{U}^2 = \mathbf{F}^\top \mathbf{F}, \quad \mathbf{B} = \mathbf{V}^2 = \mathbf{F} \mathbf{F}^\top.
\]

\(^2\)Notation: We use standard notation of modern continuum mechanics. Specifically: \( \nabla \) and Div denote the gradient and divergence with respect to the material point \( \mathbf{X} \) in the reference configuration; \( \text{grad} \) and \( \text{div} \) denote these operators with respect to the point \( \mathbf{x} = \mathbf{\chi}(\mathbf{X}, t) \) in the deformed body; a superposed dot denotes the material time-derivative. Throughout, we write \( \mathbf{F}^{-1} = (\mathbf{F}^e)^{-1}, \mathbf{F}^{p-1} = (\mathbf{F}^p)^{-1}, \) etc. We write \( \text{tr} \mathbf{A}, \text{sym} \mathbf{A}, \text{skw} \mathbf{A}, \mathbf{A}_0, \) and \( \text{sym}_0 \mathbf{A} \) 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 \( |\mathbf{A}| = \sqrt{\mathbf{A}^\top \mathbf{A}}. \)

\(^3\)Also sometimes referred to as the “intermediate” or “relaxed” local space at \( \mathbf{X} \).
Similarly, the right and left polar decompositions of $F^e$ and $F^p$ are given by
\[
F^e = R^e U^e = V^e R^e, \quad F^p = R^p U^p = V^p R^p,
\]
where $R^e$ and $R^p$ are rotations, while $U^e$, $V^e$, $U^p$, $V^p$ are symmetric, positive-definite tensors with
\[
U^e = \sqrt{F^e F^e^\top}, \quad V^e = \sqrt{F^e F^e^\top}, \quad U^p = \sqrt{F^p F^p^\top}, \quad V^p = \sqrt{F^p F^p^\top}.
\]
(2.11)
Also, the right and left elastic Cauchy-Green tensors are given by
\[
C^e = U^e U^e = F^e F^e^\top, \quad B^e = V^e V^e = F^e F^e^\top,
\]
and the right and left plastic Cauchy-Green tensors are given by
\[
C^p = U^p U^p = F^p F^p^\top, \quad B^p = V^p V^p = F^p F^p^\top.
\]
(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
\[
J^p = \det F^p = 1 \quad \text{and} \quad \text{tr} L^p = 0.
\]
(2.14)
Hence, using (2.2) and (2.14),
\[
J^e = J.
\]
(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
\[
W^p = 0.
\]
(2.16)
Then, trivially, $L^p \equiv D^p$ and
\[
\dot{F}^p = D^p F^p.
\]
(2.17)
Thus, using (2.1), (2.4), (2.5), and (2.17), we may write (2.4) for future use as
\[
(\nabla \dot{\chi}) F^{-1} = \dot{F}^e F^e^{-1} + F^e D^p F^e^{-1}.
\]
(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
\[
\chi(X, t) \rightarrow Q(t)(\chi(X, t) - o) + y(t),
\]
with $Q(t)$ a rotation (proper-orthogonal tensor), $y(t)$ a point at each $t$, and $o$ a fixed origin. Then, under a change in frame, the deformation gradient transforms according to
\[
F \rightarrow QF,
\]
(3.2)
and hence
\[
C \quad \text{is invariant;}
\]
(3.3)
also $\dot{F} \rightarrow Q \dot{F} + \dot{Q} F$, and by (2.1),
\[
L \rightarrow QLQ^\top + \dot{Q}Q^\top.
\]
(3.4)

---

Thus,
\[
D \to QDQ^\top, \quad W \to QWQ^\top + \dot{QQ}^\top.
\] (3.5)

Moreover, \(F^p F^p \to QF^p F^p\), and therefore, since observers view only the deformed configuration,
\[
F^e \to QF^e, \quad F^p \text{ is invariant},
\] (3.6)

and, by (2.5),
\[
L^e \to QL^e Q^\top + \dot{QQ}^\top,
\] (3.7)

and
\[
L^p, \quad D^p, \quad \text{and} \quad W^p \text{ are invariant}. \quad (3.8)
\]

Further, by (2.10),
\[
F^e = R^e U^e \to QF^e = QR^e U^e,
\]
\[
F^e = V^e R^e \to QF^e = QV^e Q^\top QR^e,
\]

and we may conclude from the uniqueness of the polar decomposition that
\[
R^e \to QR^e, \quad V^e \to QV^e Q^\top, \quad U^e \text{ is invariant}. \quad (3.9)
\]

Hence, from (2.12), \(B^e\) and \(C^e\) transform as
\[
B^e \to QB^e Q^\top, \quad \text{and} \quad C^e \text{ is invariant}; \quad (3.10)
\]

further, since \(F^p\) is invariant,
\[
B^p \quad \text{and} \quad C^p \text{ are also invariant}. \quad (3.11)
\]

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 \(\partial P\) of \(P\). The power expended on \(P\) by material or bodies exterior to \(P\) results from a macroscopic surface traction \(s(\mathbf{n})\), measured per unit area in the reference body, and a macroscopic body force \(b_R\), measured per unit volume in the reference body, each of whose working accompanies the macroscopic motion of the body; the body force \(b_R\) presumed to account for inertia; that is, granted the underlying frame is inertial,
\[
b_R = b_{0R} - \rho_R \ddot{\chi}, \quad (4.1)
\]

with \(b_{0R}\) the non-inertial body force and \(\rho_R\) the mass density in the reference configuration. We therefore write the external power as
\[
W_{\text{ext}}(P) = \int_{\partial P} s(\mathbf{n}) \cdot \ddot{\chi} dA + \int_P b_R \cdot \ddot{\chi} dV. \quad (4.2)
\]

We assume that power is expended internally by a stress \(P\) power-conjugate to \(\dot{F}\), an elastic stress \(T^e\)\(\) power-conjugate to \(\dot{F}^e\), and plastic stress \(T^p\) power-conjugate to \(D^p\), and we write the internal power as
\[
W_{\text{int}}(P) = \int_P (P : \dot{F} + T^e : \dot{F}^e + T^p : D^p) dV. \quad (4.3)
\]

Here \(P, \quad T^e, \quad T^p\) are defined over the body for all time. We assume that \(T^p\) is symmetric deviatoric, since \(D^p\) 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 $P : \dot{F}$ 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 total deformation gradient $F$ 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 $\chi$, $F^e$ (and hence $F$ and $F^p$) are known, and consider the fields $\dot{\chi}$, $\dot{F^e}$, and $D^p$ as virtual velocities to be specified independently in a manner consistent with the constraint (2.18). That is, denoting the virtual fields by $\dot{\chi}$, $\dot{F^e}$, and $D^p$ to differentiate them from fields associated with the actual evolution of the body, we require that

$$(\nabla \dot{\chi}) F^{-1} = \dot{F^e} F^{-1} + F^p \dot{D^p} F^{-1}. \quad (4.4)$$

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

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

consistent with (4.4). Then, writing

$$\mathcal{W}_{\text{ext}}(P, \mathcal{V}) = \int_{\partial P} s(n) \cdot \dot{\chi} \, dA + \int_P b_r \cdot \dot{\chi} \, dV,$$

$$\mathcal{W}_{\text{int}}(P, \mathcal{V}) = \int_P \left( P : (\nabla \dot{\chi} + T^e : \dot{F^e} + T^p : \dot{D^p}) \right) \, dV, \quad (4.5)$$

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 $P$,

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

**Frame-indifference of the internal power and its consequences**

We assume that the internal power $\mathcal{W}_{\text{int}}(P, \mathcal{V})$ 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

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

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

$$(\nabla \dot{\chi})^* = Q \nabla \dot{\chi} + Q \nabla \chi, \quad (\dot{F^e})^* = Q \dot{F^e} + \dot{Q} F^e,$$

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

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

$$= \int_P \left( Q^T P^* : (\nabla \dot{\chi} + \dot{Q^T} Q \nabla \chi) + Q^T T^e^* : (\dot{F^e} + \dot{Q^T} \dot{Q} F^e) + T^p^* : \dot{D^p} \right) \, dV.$$

Then (4.7) implies that

$$\int_P \left( Q^T P^* : (\nabla \dot{\chi} + \dot{Q^T} Q \nabla \chi) + Q^T T^e^* : (\dot{F^e} + \dot{Q^T} \dot{Q} F^e) + T^p^* : \dot{D^p} \right) \, dV$$

$$= \int_P \left( P : \nabla \dot{\chi} + T^e : \dot{F^e} + T^p : \dot{D^p} \right) \, dV, \quad (4.8)$$

6
or equivalently, since the part \( P \) is arbitrary,
\[
Q^* P^* : (\nabla \ddot{X} + Q^* \dot{Q} \nabla \chi) + Q^* T^{e*} : (\ddot{F}^e + Q^* \dot{Q} F^e) + T^{p*} : \ddot{D}^p = P : \nabla \ddot{X} + T^e : \ddot{F}^e + T^p : \ddot{D}^p. \tag{4.9}
\]

Also, since the change in frame is arbitrary, if we choose it such that \( \dot{Q} \) is an arbitrary time-independent rotation, so that \( \dot{Q} = 0 \), we find from (4.9) that
\[
\left( (Q^* P^*) - P \right) : \nabla \ddot{X} + \left( (Q^* T^{e*}) - T^e \right) : \ddot{F}^e + \left( T^{p*} - T^p \right) : \ddot{D}^p = 0.
\]

Since this must hold for all \( \nabla \ddot{X}, \ddot{F}^e, \) and \( \ddot{D}^p \), we find that the stresses \( P \) and \( T^e \) transform according to
\[
P^* = Q P, \quad T^{e*} = Q T^e, \tag{4.10}
\]
while \( T^p \) is invariant
\[
T^{p*} = T^p. \tag{4.11}
\]

Next, if we assume that \( Q = 1 \) at the time in question and that \( \dot{Q} \) is an arbitrary skew tensor, we find from (4.9), using (4.10), (4.11) and recalling \( F = \nabla \chi \) that
\[
\langle PF^T \rangle : \dot{Q} + \langle (T^e F^{eT}) \rangle : \dot{Q} = 0,
\]
or that the tensors \( \langle PF^T \rangle \) and \( \langle T^e F^{eT} \rangle \) are symmetric,
\[
PF^T = F P^T, \quad T^e F^{eT} = F^e T^{eT}. \tag{4.12}
\]

**Macroscopic force balance**

In applying the virtual balance (4.6) we are at liberty to choose any \( V \) consistent with the constraint (4.4). Consider a generalized virtual velocity with \( \ddot{D}^p = 0 \), so that
\[
\ddot{F}^e = (\nabla \ddot{X}) F^{e-1}. \tag{4.13}
\]

For this choice of \( V \), (4.6) yields
\[
\int_{\partial P} \mathbf{s}(n) \cdot \ddot{X} dA + \int_P \mathbf{b}_R \cdot \ddot{X} dV = \int_P \left( P + T^e F^{eT} \right) : \nabla \ddot{X} dV. \tag{4.14}
\]

Thus by defining
\[
\mathbf{T}_R \overset{\text{def}}{=} P + T^e F^{eT}, \tag{4.15}
\]
and using the divergence theorem, we may conclude that
\[
\int_{\partial P} \left( \mathbf{s}(n) - \mathbf{T}_R n \right) \cdot \ddot{X} dA + \int_P (\nabla \mathbf{T}_R + \mathbf{b}_R) \cdot \ddot{X} dV = 0.
\]

Since this relation must hold for all \( P \) and all \( \ddot{X} \), standard variational arguments yield the traction condition
\[
\mathbf{s}(n) = \mathbf{T}_R n, \tag{4.16}
\]
and the local macroscopic force balance
\[
\nabla \mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \tag{4.17}
\]
respectively. Moreover, (4.12) and (4.15) imply that
\[
\mathbf{T}_R F^T = F T^T_{R}. \tag{4.18}
\]

Thus \( \mathbf{T}_R \) 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 \( \mathbf{b}_R \) has been presumed to account for inertia, so that (4.1) is satisfied, (4.17) reduces to the local balance law for linear momentum:
\[
\nabla \mathbf{T}_R + \mathbf{b}_{0R} = \rho_R \ddot{X}, \tag{4.19}
\]
with \( \mathbf{b}_{\text{in}} \) the noninertial body force.

Further, as is standard, the Piola stress \( \mathbf{T}_h \) is related to the symmetric Cauchy stress \( \mathbf{T} \) in the deformed body by
\[
\mathbf{T}_h = J \mathbf{F}^{-\top} \mathbf{T}.
\] (4.20)

Thus,
\[
\mathbf{T} = J^{-1} \mathbf{T}_h \mathbf{F}^\top,
\] (4.21)

and using (2.15) and \( \mathbf{F}^{\epsilon \top} = \mathbf{F}^{p \top} \mathbf{F}^\top \), in (4.15) yields that the Cauchy stress admits the additive decomposition
\[
\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)},
\] (4.22)

where
\[
\mathbf{T}^{(1)} \overset{\text{def}}{=} J^{-1} \mathbf{T}^{\epsilon} \mathbf{F}^{\epsilon \top} \quad \text{and} \quad \mathbf{T}^{(2)} \overset{\text{def}}{=} J^{-1} \mathbf{P} \mathbf{F}^\top
\] (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
\[
\tilde{\chi} = 0;
\] (4.24)

also, choose the virtual field \( \tilde{\mathbf{D}}^p \) arbitrarily, and let
\[
\tilde{\mathbf{F}}^{\epsilon} = - \mathbf{F}^{\epsilon} \tilde{\mathbf{D}}^p,
\] (4.25)

consistent with (4.4). Thus
\[
\mathbf{T}^{\epsilon} : \tilde{\mathbf{F}}^{\epsilon} = -(\mathbf{F}^{\epsilon \top} \mathbf{T}^{\epsilon}) : \tilde{\mathbf{D}}^p.
\] (4.26)

Next, define a Mandel stress by
\[
\mathbf{M}^{\epsilon} \overset{\text{def}}{=} \mathbf{F}^{\epsilon \top} \mathbf{T}^{\epsilon} = J \mathbf{F}^{\epsilon \top} \mathbf{T}^{(1)} \mathbf{F}^{\epsilon - \top},
\] (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
\[
W_{\text{int}}(\mathbf{P}, \mathcal{V}) = \int_{\mathcal{P}} \left( \mathbf{T}^p - \mathbf{M}^{\epsilon} \right) : \tilde{\mathbf{D}}^p \, d\mathcal{V} = 0.
\]

Since this must be satisfied for all \( \mathbf{P} \) and all symmetric and deviatoric tensors \( \tilde{\mathbf{D}}^p \), a standard argument yields the microforce balance
\[
\text{sym}_0 \mathbf{M}^{\epsilon} = \mathbf{T}^p.
\] (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;

- \( \mathbf{\epsilon}_h \) and \( \mathbf{\eta}_h \) represent the internal energy and entropy densities, measured per unit volume in the reference body;

- \( \mathbf{q}_h \) denote the heat flux, measured per unit area in the reference body; and

- \( q_h \) 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
\[
\dot{\varepsilon}_r dV = - \int_{\partial P} \mathbf{q}_r \cdot \mathbf{n} dA + \int_P \mathbf{q}_r dV + \mathcal{W}_{\text{ext}}(\mathbf{P}),
\]  
while the second law takes the form of an entropy imbalance
\[
\dot{\eta}_n dV \geq - \int_{\partial P} \frac{\mathbf{q}_r \cdot \mathbf{n}}{\vartheta} dA + \int_P \frac{\mathbf{q}_r}{\vartheta} dV.
\]  
Thus, since \( \mathcal{W}_{\text{ext}}(\mathbf{P}) = \mathcal{W}_{\text{int}}(\mathbf{P}) \) and since \( \mathbf{P} \) is arbitrary, we may use (4.3) to obtain local forms of (5.1) and (5.2):
\[
\begin{align*}
\dot{\varepsilon}_r &= - \text{Div} \mathbf{q}_r + q_r + \mathbf{P} : \dot{\mathbf{F}} + \mathbf{T}^e : \dot{\mathbf{F}}^e + \mathbf{T}^p : \mathbf{D}^p, \\
\dot{\eta}_n &\geq - \frac{1}{\vartheta} \text{Div} \mathbf{q}_r + \frac{1}{\vartheta^2} q_r \cdot \nabla \vartheta + \frac{q_r}{\vartheta}.
\end{align*}
\]  
Let
\[
\psi_r \overset{\text{def}}{=} \varepsilon_r - \vartheta \eta_n
\]  
denote the (Helmholtz) free energy per unit volume of the reference body. Then (5.3) yields the local free-energy imbalance
\[
\dot{\psi}_r + \eta_n \dot{\vartheta} + \frac{1}{\vartheta} \mathbf{q}_r \cdot \nabla \vartheta - \mathbf{P} : \dot{\mathbf{F}} - \mathbf{T}^e : \dot{\mathbf{F}}^e - \mathbf{T}^p : \mathbf{D}^p \leq 0.
\]  
**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),
\[
\mathbf{T}^e = \mathbf{J} \mathbf{T}^{(1)} \mathbf{F}^e - \mathbf{T}^{(2)} \mathbf{F}^e - \mathbf{T}^p : \mathbf{D}^p.
\]  
We introduce two new stress measures
\[
\mathbf{S}^e \overset{\text{def}}{=} \mathbf{F}^e - \frac{1}{2} \mathbf{F}^e : \mathbf{F}^e = \mathbf{J} \mathbf{T}^{(1)} \mathbf{F}^e - \mathbf{T}^{(2)} \mathbf{F}^e - \mathbf{T}^p : \mathbf{D}^p.
\]  
which are symmetric, since \( \mathbf{T}^{(1)} \) and \( \mathbf{T}^{(2)} \) are symmetric. Thus \( \mathbf{S}^e \) 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
\[
\mathbf{M}^e = \mathbf{C}^e \mathbf{S}^e.
\]  
Next, differentiating (2.9)\(_1\) results in the following expression for the rate of change of \( \mathbf{C} \),
\[
\dot{\mathbf{C}} = \mathbf{F}^\top \dot{\mathbf{F}} + \mathbf{F}^\top \dot{\mathbf{F}}.
\]  
Hence, since \( \mathbf{S} \) is symmetric,
\[
\mathbf{S} : \dot{\mathbf{C}} = 2 \mathbf{S} : \mathbf{F}^\top \dot{\mathbf{F}} = 2 (\mathbf{FS}) : \dot{\mathbf{F}},
\]  
or, using (5.7)\(_2\), we obtain
\[
\mathbf{P} : \dot{\mathbf{F}} = \frac{1}{2} \mathbf{S} : \dot{\mathbf{C}}.
\]  
In an entirely analogous manner,
\[
\mathbf{T}^e : \dot{\mathbf{F}}^e = \frac{1}{2} \mathbf{S}^e : \dot{\mathbf{C}}.
\]  
Then, from (4.3), (5.9) and (5.10), we note that the internal power per unit volume of the reference body is
\[
\frac{1}{2} \mathbf{S}^e : \dot{\mathbf{C}} + \frac{1}{2} \mathbf{S} : \dot{\mathbf{C}} + \mathbf{T}^p : \mathbf{D}^p.
\]
Thus, the energy balance (5.3) may be written as
\[
\dot{\varepsilon}_R = -\text{Div} \mathbf{q}_R + q_R + \frac{1}{2} \mathbf{S}^e : \dot{\mathbf{C}}^e + \frac{1}{2} \mathbf{S} : \dot{\mathbf{C}} + \mathbf{T}^p : \mathbf{D}^p, \tag{5.12}
\]
while the free-energy imbalance (5.5) becomes
\[
\dot{\psi}_R + \eta_R \dot{\vartheta} + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla \vartheta - \frac{1}{2} \mathbf{S}^e : \dot{\mathbf{C}}^e - \frac{1}{2} \mathbf{S} : \dot{\mathbf{C}} - \mathbf{T}^p : \mathbf{D}^p \leq 0. \tag{5.13}
\]

Finally, we note that \( \psi_R, \eta_R \) and \( \vartheta \) 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
\[
\mathbf{C}, \mathbf{C}^e, \mathbf{B}^p, \mathbf{D}^p, \mathbf{S}, \mathbf{S}^e, \mathbf{T}^p, \text{ and } \mathbf{M}^e, \tag{5.14}
\]
are also invariant, as are the fields
\[
\mathbf{q}_R, \nabla \vartheta, \tag{5.15}
\]
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
  \[
  \xi = (\xi_1, \xi_2, \ldots, \xi_m).
  \]
  Since \( \xi \) 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:\(^6\)
\[
\begin{aligned}
\psi_R &= \tilde{\psi}^{(1)}(\mathbf{C}^e, \vartheta) + \tilde{\psi}^{(2)}(\mathbf{C}, \vartheta) + \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta), \\
\eta_R &= \tilde{\eta}^{(1)}(\mathbf{C}^e, \vartheta) + \tilde{\eta}^{(2)}(\mathbf{C}, \vartheta) + \tilde{\eta}^{(p)}(\mathbf{A}, \vartheta), \\
\mathbf{S}^e &= \tilde{\mathbf{S}}(\mathbf{C}^e, \vartheta), \\
\mathbf{S} &= \tilde{\mathbf{S}}(\mathbf{C}, \vartheta), \\
\mathbf{T}^p &= \tilde{\mathbf{T}}^p(\mathbf{D}^p, \Lambda), \\
\dot{\xi}_i &= \tilde{h}_i(\mathbf{D}^p, \Lambda), \\
\dot{\mathbf{A}} &= \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\Lambda) \mathbf{d}^p, \quad \mathbf{d}^p \overset{\text{def}}{=} |\mathbf{D}^p|.
\end{aligned}
\tag{6.1}
\]

\(^5\)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 $\mathbf{A}$ denotes the list
\[
\mathbf{A} = (\mathbf{C}^e, \mathbf{B}^p, \mathbf{A}, \mathbf{\xi}, \vartheta).
\] (6.2)

To the constitutive equations (6.1), we append a simple Fourier’s relation for the heat flux,
\[
\mathbf{q}_{in} = -K(\vartheta) \nabla \vartheta,
\] (6.3)

where $K$ 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 $(\mathbf{\xi}, \mathbf{A})$ are also invariant, the constitutive equations (6.1) and (6.3) are frame-indifferent.

In (6.1), $\dot{\psi}^{(1)}$ is an energy associated with intermolecular interactions and modeled using the elastic Cauchy-Green tensor $\mathbf{C}^e = \mathbf{F}^{ce} \mathbf{F}^{ce}$, $\dot{\psi}^{(2)}$ an energy associated with the stretching of the polymer chains and modeled using the total Cauchy-Green tensor $\mathbf{C} = \mathbf{F}^p \mathbf{F}^p$, and $\dot{\psi}^{(p)}$ 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) for $\mathbf{A}$, the term $\mathbf{G}(\mathbf{A}) d^p$ 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 $\mathbf{W}^p = 0$,
\[
\dot{\mathbf{B}}^p = \mathbf{D}^p \mathbf{B}^p + \mathbf{B}^p \dot{\mathbf{D}}^p.
\] (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 $\mathbf{G}(\mathbf{A}) \neq 0$, and thus in general $\mathbf{A}$ is not the same as $\mathbf{B}^p$. Since $\det \mathbf{A} = 1$, the evolution equation (6.1) for $\mathbf{A}$ must satisfy $\text{tr} (\mathbf{A} \mathbf{A}^{-1}) = 0$, and hence the recovery function $\mathbf{G}(\mathbf{A})$ is constrained to satisfy $\text{tr} (\mathbf{G}(\mathbf{A}) \mathbf{A}^{-1}) = 0$. The evolution equation (6.1) represents a generalization of the non-linear kinematic-hardening rule (Armstrong and Frederick, 1966) of the small deformation theory of classical metal viscoplasticity, but here applied to polymer-viscoplasticity.

**Remark 2:** The evolution equation for $\mathbf{A}$ may be further generalized to read
\[
\dot{\mathbf{A}} = \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\mathbf{A}) d^p - \mathbf{G}_{\text{static}}(\mathbf{A}),
\]
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 $\mathbf{B}^p_{\text{en}} = \mathbf{F}^p_{\text{en}} \mathbf{F}^{p\top}_{\text{en}}$, where $\mathbf{F}^p_{\text{en}}$ is an “energetic” part of $\mathbf{F}^p$ introduced via a decomposition $\mathbf{F}^p = \mathbf{F}^p_{\text{en}} \mathbf{F}^p_{\text{dis}}$, see Henann and Anand (2008). For a detailed discussion of the relationship of $\mathbf{A}$ to $\mathbf{B}^p_{\text{en}}$, see Chen and Anand (2008).

### 6.1 Thermodynamic restrictions

From (6.1)
\[
\dot{\psi}_{\text{en}} = \frac{\partial \tilde{\psi}^{(1)}(\mathbf{C}^e, \vartheta)}{\partial \mathbf{C}^e} : \mathbf{C}^e + \frac{\partial \tilde{\psi}^{(1)}(\mathbf{C}^e, \vartheta)}{\partial \vartheta} : \dot{\vartheta} + \frac{\partial \tilde{\psi}^{(2)}(\mathbf{C}, \vartheta)}{\partial \mathbf{C}} : \dot{\mathbf{C}} + \frac{\partial \tilde{\psi}^{(2)}(\mathbf{C}, \vartheta)}{\partial \vartheta} : \dot{\vartheta} + \frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \dot{\mathbf{A}} + \frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \vartheta} : \dot{\vartheta},
\]
and, using (6.1) and the symmetry of $\mathbf{A}$ and $\partial \tilde{\psi}/\partial \mathbf{A}$,
\[
\frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \dot{\mathbf{A}} = \frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \left( \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - \mathbf{G}(\mathbf{A}) d^p \right)
\]
\[
= 2 \left( 2 \left( \frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \mathbf{A}} : \mathbf{A} \right)_0 \right) : \mathbf{D}^p - \frac{\partial \tilde{\psi}^{(p)}(\mathbf{A}, \vartheta)}{\partial \vartheta} : \mathbf{G}(\mathbf{A}) d^p.
\]

\[\text{Cf., e.g., Chaboche (2008) for a recent review of the large variety of kinematic-hardening rules in classical small deformation metal-viscoplasticity.}\]
Hence, satisfaction of the free-energy imbalance (5.13) requires that the constitutive equations (6.1) and (6.3) satisfy
\[
\left(\frac{1}{2} S^e(C^e, \vartheta) - \frac{\partial \tilde{\psi}^{(1)}(C^e, \vartheta)}{\partial C^e}\right) \dot{C}^e + \left(\frac{1}{2} S(C, \vartheta) - \frac{\partial \tilde{\psi}^{(2)}(C, \vartheta)}{\partial C}\right) \dot{C} - \left(\tilde{\eta}^{(1)}(C^e, \vartheta) + \frac{\partial \tilde{\psi}^{(1)}(C^e, \vartheta)}{\partial \vartheta}\right) \dot{\vartheta} - \left(\tilde{\eta}^{(2)}(C, \vartheta) + \frac{\partial \tilde{\psi}^{(2)}(C, \vartheta)}{\partial \vartheta}\right) \dot{\vartheta} - \left(\tilde{\eta}^{(p)}(A, \vartheta) + \frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial \vartheta}\right) \dot{\vartheta} + \left( T^p(D^p, A) - 2\left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A}\right)_0 \right) : D^p + \left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A} : G(A)\right) d^p \geq 0
\]
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 \(S^e\) and \(S\) via the stress relations
\[
S^e(C^e, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(1)}(C^e, \vartheta)}{\partial C^e},
\]
\[
S(C, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(2)}(C, \vartheta)}{\partial C},
\]
and the components \(\eta^{(1)}, \eta^{(2)},\) and \(\eta^{(p)}\) of the entropy \(\eta_h\) via the entropy relations
\[
\eta^{(1)}(C^e, \vartheta) = - \frac{\partial \tilde{\psi}^{(1)}(C^e, \vartheta)}{\partial \vartheta},
\]
\[
\eta^{(2)}(C, \vartheta) = - \frac{\partial \tilde{\psi}^{(2)}(C, \vartheta)}{\partial \vartheta},
\]
\[
\eta^{(p)}(A, \vartheta) = - \frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial \vartheta};
\]

(ii) the plastic distortion-rate \(D^p\) and the temperature gradient \(\nabla \vartheta\) satisfy the reduced dissipation inequality
\[
\left( T^p(D^p, A) - 2\left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A}\right)_0 \right) : D^p + \left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A} : G(A)\right) d^p \geq 0.
\]

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
\[
Y^p(D^p, A) : D^p + \left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A} : G(A)\right) d^p > 0,
\]
whenever \(D^p \neq 0\), where we have introduced a symmetric and deviatoric dissipative flow stress \(Y^p\) defined by
\[
Y^p(D^p, A) \overset{\text{def}}{=} \tilde{T}^p(D^p, A) - 2\left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A}\right)_0;
\]
and that the material also separately satisfies the heat conduction inequality
\[
\frac{1}{\vartheta} \nabla \vartheta \cdot K(\vartheta) \nabla \vartheta > 0 \quad \text{whenever} \quad \nabla \vartheta \neq 0.
\]

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

From (6.11) we note that the stress \(T^p\), which is conjugate to \(D^p\), may be split into a dissipative part and an energetic part as follows:
\[
T^p = T^p(D^p, A) = \underbrace{Y^p(D^p, A)}_{\text{dissipative part of } T^p} + 2\left(\frac{\partial \tilde{\psi}^{(p)}(A, \vartheta)}{\partial A}\right)_0 \underbrace{\overbrace{\text{energetic part of } T^p}}_{\text{energetic part of } T^p}.
\]

\(^8\)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,

\[ \dot{\psi}_R = \frac{1}{2} S^c : \dot{C}^c + \frac{1}{2} S : \dot{C} - \eta_R \dot{\theta} + 2 \left( \frac{\partial \tilde{\psi}(p)}{\partial A} \right)_\theta : D^p - \left( \frac{\partial \tilde{\psi}(p)}{\partial A} : G(A) \right) d^p, \]  

(6.14)

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

\[ \dot{\epsilon}_R = \frac{\partial \eta_R}{\partial \theta} + \frac{1}{2} S^c : \dot{C}^c + \frac{1}{2} S : \dot{C} + 2 \left( \frac{\partial \tilde{\psi}(p)}{\partial A} \right)_\theta : D^p - \left( \frac{\partial \tilde{\psi}(p)}{\partial A} : G(A) \right) d^p. \]  

(6.15)

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

\[ \dot{\psi}_R = -\text{Div} q_R + q_R + Y^p(D^p, A) : D^p + \left( \frac{\partial \tilde{\psi}(p)(A, \theta)}{\partial A} : G(A) \right) d^p. \]  

(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

\[ \psi_R = \tilde{\psi}^{(1)}(C^c, \theta) + \tilde{\psi}^{(2)}(C, \theta) + \tilde{\psi}(p)(A, \theta) \equiv \tilde{\psi}(C^c, C, A, \theta), \]

\[ \eta_R = \tilde{\eta}^{(1)}(C^c, \theta) + \tilde{\eta}^{(2)}(C, \theta) + \tilde{\eta}(p)(A, \theta) \equiv \tilde{\eta}(C^c, C, A, \theta), \]  

(6.17)

then the internal energy density is given by

\[ \epsilon_R = \tilde{\epsilon}(C^c, C, A, \theta) \overset{\text{def}}{=} \tilde{\psi}(C^c, C, A, \theta) + \partial \tilde{\eta}(C^c, C, A, \theta), \]  

(6.18)

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

\[ c \overset{\text{def}}{=} \frac{\partial \tilde{\psi}(C^c, C, A, \theta)}{\partial \theta}. \]  

(6.19)

Hence, from (6.18)

\[ c \overset{\text{def}}{=} \left( \frac{\partial \tilde{\psi}(C^c, C, A, \theta)}{\partial \theta} + \tilde{\eta}(C^c, C, A, \theta) + \theta \frac{\partial \tilde{\psi}(C^c, A, \theta)}{\partial \theta} \right), \]  

(6.20)

and use of (6.8) and (6.17) gives

\[ c \overset{\text{def}}{=} -\theta \frac{\partial^2 \tilde{\psi}(C^c, C, A, \theta)}{\partial \theta^2} = -\theta \left( \frac{\partial^2 \tilde{\psi}^{(1)}(C^c, \theta)}{\partial \theta^2} + \frac{\partial^2 \tilde{\psi}^{(2)}(C, \theta)}{\partial \theta^2} + \frac{\partial^2 \tilde{\psi}(p)(A, \theta)}{\partial \theta^2} \right). \]  

(6.21)

Next, from (6.8) and (6.21)

\[ \dot{\theta_R} = -\theta \frac{\partial \tilde{\psi}^{(1)}(C^c, \theta)}{\partial \theta} : \dot{C}^c - \theta \frac{\partial \tilde{\psi}^{(2)}(C, \theta)}{\partial \theta} : \dot{C} - \theta \frac{\partial \tilde{\psi}(p)(A, \theta)}{\partial \theta} : \dot{A} + c \dot{\theta}. \]  

(6.22)

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

\[ c \dot{\theta} = -\text{Div} q_R + q_R + Y^p(D^p, A) : D^p + \left( \frac{\partial \tilde{\psi}(p)(A, \theta)}{\partial A} : G(A) \right) d^p \]

\[ + \theta \frac{\partial^2 \tilde{\psi}^{(1)}(C, \theta)}{\partial \theta^2} : \dot{C} + \theta \frac{\partial^2 \tilde{\psi}^{(2)}(C, \theta)}{\partial \theta^2} : \dot{C} + \theta \frac{\partial \tilde{\psi}(p)(A, \theta)}{\partial \theta} : \dot{A}. \]  

(6.23)
6.3 Isotropy

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

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

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

(ii) the symmetry group $\mathcal{G}_I$ 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

$$S \colon \dot{C}, \quad S \colon \dot{\bar{C}}, \quad \text{and} \quad T^p : D^p \text{ be invariant.} \quad (6.24)$$

6.3.1 Isotropy of the reference space

Let $Q$ be a time-independent rotation of the reference configuration. Then $F \rightarrow FQ$, and hence

$$C \rightarrow Q^\top CQ, \quad F^p \rightarrow F^p Q, \quad \text{and} \quad \dot{F}^e \text{ is invariant, and hence} \ C^e \text{ and } B^p \text{ are invariant,} \quad (6.25)$$

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

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

We may therefore use $(6.24)$ to conclude that

$$S \rightarrow Q^\top SQ, \quad \text{while} \ S^e \text{ and } T^p \text{ are invariant.} \quad (6.26)$$

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

$$\begin{align*}
\bar{\psi}^{(2)}(C, \vartheta) &= \bar{\psi}^{(2)}(Q^\top CQ, \vartheta), \\
\bar{\eta}^{(2)}(C, \vartheta) &= \bar{\eta}^{(2)}(Q^\top CQ, \vartheta), \\
Q^\top \bar{S}(C, \vartheta)Q &= \bar{S}(Q^\top CQ, \vartheta),
\end{align*} \quad (6.27)$$

for all symmetric positive definite tensors $C$, and all rotations $Q \in \mathcal{G}_R$.

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 $Q$ for the reference configuration, the temperature gradient $\nabla \vartheta$ and the heat flux $q_R$ transform as

$$\nabla \vartheta \rightarrow Q^\top \nabla \vartheta, \quad q_R \rightarrow Q^\top q_R.$$

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

$$K(\vartheta) = Q^\top K(\vartheta)Q \quad (6.28)$$

for all rotations $Q$ in the symmetry group $\mathcal{G}_R$.

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

$$\mathcal{G}_R = \text{Orth}^+ \quad (6.29)$$

so that the response of the material is invariant under arbitrary rotations of the reference space. Henceforth...
In this case, the response functions $\hat{\psi}^{(2)}$, $\hat{\eta}^{(2)}$, and $\hat{S}$, must each be isotropic, and that the thermal conductivity has the representation

$$K(\vartheta) = \kappa(\vartheta)I, \quad \text{with} \quad \kappa(\vartheta) > 0$$

(6.30)
a scalar thermal conductivity.

### 6.3.2 Isotropy of the intermediate structural space

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

$$F^c \rightarrow F^c Q \quad \text{and} \quad F^p \rightarrow Q^\top F^p,$$

(6.31)
and also

$$C^c \rightarrow Q^\top C^c Q, \quad B^p \rightarrow Q^\top B^p Q, \quad \dot{C}^c \rightarrow Q^\top \dot{C}^c Q, \quad D^p \rightarrow Q^\top D^p Q.$$  

(6.32)
Further, since the tensor $A$ maps vectors in the intermediate space into vectors in the same space, we assume that $A$ transforms as

$$A \rightarrow Q^\top A Q,$$

and hence

$$\hat{A} \rightarrow Q^\top \hat{A} Q.$$

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

$$S^c \rightarrow Q^\top S^c Q, \quad T^p \rightarrow Q^\top T^p Q.$$  

(6.33)
Thus, with reference to the constitutive equations (6.1) we conclude that

$$\begin{aligned}
\hat{\psi}^{(1)}(C^c, \vartheta) &= \hat{\psi}^{(1)}(Q^\top C^c Q, \vartheta), \quad \hat{\psi}^{(p)}(A, \vartheta) = \hat{\psi}^{(p)}(Q^\top A Q, \vartheta), \\
\hat{\eta}^{(1)}(C^c, \vartheta) &= \hat{\eta}^{(1)}(Q^\top C^c Q, \vartheta), \quad \hat{\eta}^{(p)}(A, \vartheta) = \hat{\eta}^{(p)}(Q^\top A Q, \vartheta), \\
Q^\top S^c(C^c, \vartheta)Q &= S^c(Q^\top C^c Q, \vartheta), \\
Q^\top T^p(D^p, \Lambda)Q &= T^p(Q^\top D^p Q, Q^\top \Lambda Q), \\
h_i(D^p, \Lambda) &= h_i(Q^\top D^p Q, Q^\top \Lambda Q), \\
Q^\top G(D^p, \Lambda)Q &= G(Q^\top D^p Q, Q^\top \Lambda Q),
\end{aligned}$$

(6.34)
with

$$Q^\top \Lambda Q = (Q^\top C^c Q, Q^\top B^p Q, Q^\top A Q, \xi, \vartheta),$$

must hold for all rotations $Q$ in the symmetry group $G_t$ 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,

$$G_t = \text{Orth}^+,$$

(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 $\hat{\psi}^{(2)}$, $\hat{\eta}^{(2)}$, and $\hat{S}$ from isotropy of the reference space, (‡) the response functions $\hat{\psi}^{(1)}$, $\hat{\psi}^{(p)}$, $\hat{\eta}^{(1)}$, $\hat{\eta}^{(p)}$, $\hat{S}^c$, $T^p$, $h_i$, and $G$ must also each be isotropic.
6.4 Consequences of isotropy of the free energy

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

$$\tilde{\psi}^{(1)}(C^e, \vartheta) = \tilde{\psi}^{(1)}(I_{C^e}, \vartheta),$$  \hspace{1cm} (6.36)

where

$$I_{C^e} = \left( I_1(C^e), I_2(C^e), I_3(C^e) \right)$$

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

$$S^e = \tilde{S}^e(C^e, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(1)}(I_{C^e}, \vartheta)}{\partial C^e},$$  \hspace{1cm} (6.37)

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

$$M^e = C^e S^e,$$

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

$$C^e S^e = S^e C^e,$$  \hspace{1cm} (6.38)

and hence that the Mandel stress $M^e$ is symmetric.

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

$$\tilde{\psi}^{(2)}(C, \vartheta) = \tilde{\psi}^{(2)}(I_C, \vartheta),$$  \hspace{1cm} (6.39)

and from (6.7),

$$S = \tilde{S}(C, \vartheta) = 2 \frac{\partial \tilde{\psi}^{(2)}(I_C, \vartheta)}{\partial C}.$$  \hspace{1cm} (6.40)

Further the defect free energy has a representation

$$\tilde{\psi}^{(p)} = \tilde{\psi}^{(p)}(I_A, \vartheta)$$  \hspace{1cm} (6.41)

and this yields that

$$\frac{\partial \tilde{\psi}^{(p)}(I_A, \vartheta)}{\partial A} A,$$  \hspace{1cm} (6.42)

is a symmetric tensor.

7 Flow rule

Recall from (6.13) that the constitutive equation for $T^p$ is

$$T^p = 2 \left( \frac{\partial \tilde{\psi}^{(p)}(I_A, \vartheta)}{\partial A} A \right)_0 + Y^p(D^p, A).$$  \hspace{1cm} (7.1)

We denote the energetic part of $T^p$ by

$$M_{\text{back}} \defeq 2 \left( \frac{\partial \tilde{\psi}^{(p)}(I_A, \vartheta)}{\partial A} A \right)_0,$$  \hspace{1cm} (7.2)

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

$$M_{\text{eff}} \defeq M^e - M_{\text{back}}.$$  \hspace{1cm} (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

$$(M_{\text{eff}})_0 = Y^p(D^p, A).$$  \hspace{1cm} (7.4)

We now make two major assumptions concerning the plastic flow for isotropic materials:
Let
\[ N_p \equiv \frac{D_p}{dP} \]  
(7.5)
denote the direction of plastic flow whenever \( D_p \neq 0 \), then the mechanical dissipation inequality (6.10) may be written as
\[ \left( Y_p(d_p, N_p, \Lambda) : N_p + \left( \frac{\partial \psi(p)(A, \theta)}{\partial A} : G(\Lambda) \right) \right) dP > 0 \quad \text{when} \quad D_p \neq 0. \]  
(7.6)
Guided by (7.6), we assume henceforth that the dissipative flow stress \( Y_p \) is parallel to and points in the same direction as \( N_p \), so that
\[ Y_p(d_p, N_p, \Lambda) = Y(d_p, N_p, \Lambda) N_p, \]  
(7.7)
where
\[ Y(d_p, N_p, \Lambda) = Y_p(d_p, N_p, \Lambda) : N_p \]  
(7.8)
represents a scalar flow strength of the material.

(2) We also assume that the scalar flow strength \( Y(d_p, N_p, \Lambda) \) and the function \( h_i(d_p, N_p, \Lambda) \) characterizing the evolution of the scalar internal variable \( \xi_i \) are independent of the flow direction \( N_p \), so that
\[ Y(d_p, \Lambda), \quad h_i(d_p, \Lambda). \]  
(7.9)
Thus, using (7.9) and (7.7), the flow rule (7.4) reduces to,
\[ (M_{\text{eff}}^e)_0 = Y(d_p, \Lambda) N_p \]  
(7.10)
which immediately gives
\[ N_p = \frac{(M_{\text{eff}}^e)_0}{|(M_{\text{eff}}^e)_0|}, \]  
(7.11)
and
\[ |(M_{\text{eff}}^e)_0| = Y(d_p, \Lambda). \]  
(7.12)
When \( |(M_{\text{eff}}^e)_0| \) and \( \Lambda \) are known, (7.12) serves as an implicit equation for the scalar flow rate \( d_p \).

Finally, using (7.8), (7.9) and (7.12), the mechanical dissipation inequality (7.6) reduces to
\[ \left( |(M_{\text{eff}}^e)_0| + \left( \frac{\partial \psi(p)(I_A, \theta)}{\partial A} : G(\Lambda) \right) \right) dP > 0 \quad \text{when} \quad d_p \neq 0. \]  
(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:

\[ ^9 \text{This assumption corresponds to the classical notion of maximal dissipation in Mises-type theories of metal plasticity.} \]
\[ x = \chi(X, t), \quad \text{motion}; \]
\[ F = \nabla X, \quad J = \det F > 0, \quad \text{deformation gradient}; \]
\[ F = F^e F^p, \quad \text{elastic-plastic decomposition of } F; \]
\[ F^e, \quad J^e = \det F^e = J > 0, \quad \text{elastic distortion}; \]
\[ F^p, \quad J^p = \det F^p = 1, \quad \text{inelastic distortion}; \]
\[ F^e = R^e U^e, \quad \text{polar decomposition of } F^e; \]
\[ C = F^\top F, \quad \text{right Cauchy-Green tensor}; \]
\[ C^e = F^e \top F^e, \quad \text{elastic right Cauchy-Green tensors}; \]
\[ B^p = F^p F^p \top, \quad \text{plastic left Cauchy-Green tensor}; \]
\[ T = T^\top, \quad \text{Cauchy stress}; \]
\[ T_\kappa = JTF^{-\top}, \quad \text{Piola stress}; \]
\[ \psi, \quad \text{free energy density per unit reference volume}; \]
\[ \eta, \quad \text{entropy density per unit reference volume}; \]
\[ \xi = (\xi_1, \xi_2, \ldots, \xi_m) \quad m \text{ scalar internal variables}; \]
\[ A, \quad A = A^\top, \quad \det A = 1 \quad \text{tensorial internal variable}; \]
\[ \vartheta > 0, \quad \text{absolute temperature}; \]
\[ \nabla \vartheta, \quad \text{referential temperature gradient}; \]
\[ q_\kappa, \quad \text{referential heat flux vector}. \]

### 8.1 Constitutive equations

1. **Free energy**
   \[
   \psi = \psi^{(1)}(I_C^e, \vartheta) + \psi^{(2)}(I_C, \vartheta) + \psi^{(p)}(I_A, \vartheta),
   \]  
   where \( I_C^e, I_C, \) and \( I_C \) are the lists of the principal invariants of \( C^e, C, \) and \( A, \) respectively.

2. **Cauchy stress**
   \[
   T = T^{(1)} + T^{(2)},
   \]  
   with
   \[
   T^{(1)} \equiv J^{-1} \left( F^e S^e F^e \top \right), \quad S^e = 2 \frac{\partial \tilde{\psi}^{(1)}(I_C^e, \vartheta)}{\partial C^e},
   \]  
   and
   \[
   T^{(2)} \equiv J^{-1} \left( F S F \top \right), \quad S = 2 \frac{\partial \tilde{\psi}^{(2)}(I_C, \vartheta)}{\partial C}. \]

3. **Driving stresses for plastic flow**
   With
   \[
   M^e = C^e S^e,
   \]  
   denoting the *symmetric* Mandel stress,
   \[
   M_{\text{back}} = 2 \left( \frac{\partial \tilde{\psi}^{(p)}(I_A, \vartheta)}{\partial A} \right) A_0,
   \]  
   a *symmetric deviatoric* back-stress, and
   \[
   M^e = M^e - M_{\text{back}} \quad \text{an effective Mandel stress.}
   \]  
   The driving stress for plastic flow is taken as the stress difference
   \[
   (M^e)_{\text{eff}} = M^e_0 - M_{\text{back}}, \]
   which is the symmetric and deviatoric.
The evolution equation for \( F^p \) is

\[
\dot{F}^p = D^p F^p,
\]

with \( D^p \) given by

\[
D^p = d^p N^p, \quad N^p = \frac{(M^e^p)_{\Omega}}{|(M^e^p)|},
\]

where with

\[
\Lambda \overset{\text{def}}{=} \{ C^e, B^p, A, \xi, \vartheta \},
\]

the scalar flow rate \( dp \) is obtained by solving the scalar strength relation

\[
|M^e^p| = Y(dp, \Lambda),
\]

for given \((M^e^p)_{\Omega} \) and \( \Lambda \), where the strength function \( Y(dp, \Lambda) \) is an isotropic function of its arguments.

The evolution equations for internal variables

\[
\begin{cases}
\dot{\xi}_i = h_i(dp, \Lambda), \\
\dot{\Lambda} = D^p \Lambda + AD^p - G(\Lambda) dp^p,
\end{cases}
\]

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

The evolution equations for \( F^p, \xi \) and \( A \) 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

\[
F(X, 0) = F^p(X, 0) = A(X, 0) = 1, \quad \xi_i(X, 0) = \xi_{i,0} \text{ (constant)},
\]

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

Finally, we have the entropy relation

\[
\eta_R = - \left( \frac{\partial \hat{\psi}^{(1)}(I_C, \vartheta)}{\partial \vartheta} + \frac{\partial \hat{\psi}^{(2)}(I_C, \vartheta)}{\partial \vartheta} + \frac{\partial \hat{\psi}^{(p)}(I_A, \vartheta)}{\partial \vartheta} \right),
\]

together with Fourier’s law

\[
q_R = -\kappa \nabla \vartheta,
\]

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)),

\[
\text{Div} \mathbf{T}_R + \mathbf{b}_R = \rho_0 \ddot{\chi},
\]

where \( \mathbf{b}_R \) is the non-inertial body force, \( \rho_0 \) is the mass density in the reference body, and \( \ddot{\chi} \) is the acceleration.

The specific heat in the theory is given by

\[
c \overset{\text{def}}{=} -\vartheta \left( \frac{\partial^2 \hat{\psi}^{(1)}(I_C, \vartheta)}{\partial \vartheta^2} + \frac{\partial^2 \hat{\psi}^{(2)}(I_C, \vartheta)}{\partial \vartheta^2} + \frac{\partial^2 \hat{\psi}^{(p)}(I_A, \vartheta)}{\partial \vartheta^2} \right),
\]

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

\[
c \vartheta = -\text{Div} q_R + q_R + \left( |(M^e^p)_{\Omega}| + \left( \frac{\partial \hat{\psi}^{(p)}(I_A, \vartheta)}{\partial A} : G(\Lambda) \right) \right) dp^p

+ \frac{1}{c} \frac{\partial S\dot{}^{(e)}}{\partial \vartheta} : \dot{C}^e + \frac{1}{c} \frac{\partial S\dot{}^{(p)}}{\partial \vartheta} : \dot{C} + \vartheta \frac{\partial \hat{\psi}^{(p)}(I_A, \vartheta)}{\partial \vartheta^\Lambda} : \dot{\Lambda}.
\]

(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.

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