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A theory of amorphous solids undergoing large deformations, with application to polymeric glasses

Lallit Anand ^{a,*}, Morton E. Gurtin ^{b,1}

^a Department of Mechanical Engineering, Massachusetts Institute of Technology, Room 1-310, Cambridge, MA 02139, USA

^b Department of Mathematical Sciences, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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Abstract

This paper develops a continuum theory for the elastic–viscoplastic deformation of amorphous solids such as polymeric and metallic glasses. Introducing an internal-state variable that represents the local free-volume associated with certain metastable states, we are able to capture the highly non-linear stress–strain behavior that precedes the yield-peak and gives rise to post-yield strain softening. Our theory explicitly accounts for the dependence of the Helmholtz free energy on the plastic deformation in a thermodynamically consistent manner. This dependence leads directly to a backstress in the underlying flow rule, and allows us to model the rapid strain-hardening response after the initial yield-drop in monotonic deformations, as well as the Bauschinger-type reverse-yielding phenomena typically observed in amorphous polymeric solids upon unloading after large plastic deformations. We have implemented a special set of constitutive equations resulting from the general theory in a finite-element computer program. Using this finite-element program, we apply the specialized equations to model the large-deformation response of the amorphous polymeric solid polycarbonate, at ambient temperature and pressure. We show numerical results to some representative problems, and compare them against corresponding results from physical experiments.

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1. Introduction

Under certain conditions many solids appear in a disordered form; such solids are referred to as *amorphous* or *glassy*. Important examples of amorphous solids are polymeric (molecular) glasses and metallic (atomic) glasses. While there are important differences in the microstructural mechanisms leading

* Corresponding author. Tel.: +1-617-253-1635; fax: +1-617-258-8742.

E-mail addresses: anand@mit.edu (L. Anand), mg0c@andrew.cmu.edu (M.E. Gurtin).

¹ Tel.: +1-412-268-6380.

to plastic or inelastic deformations of polymeric and metallic amorphous solids,² it is possible to develop a reasonably general constitutive framework for the inelastic deformation of such amorphous solids at the macroscopic level. The purpose of this paper is to formulate a macroscopic theory for the elastic–visco-plastic deformation of an amorphous solid under isothermal conditions below its *glass transition temperature*.

A significant advance in modeling the plastic deformation of amorphous polymers has been made by Parks, Argon, Boyce, Arruda, and their co-workers (e.g. Parks et al., 1985; Boyce et al., 1988; Arruda and Boyce, 1993b), and by Wu and Van der Giessen (1993). Our theory is based on physical ideas contained in these models, and, following these authors, we utilize the Kröner–Lee decomposition, $\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$, of the deformation gradient \mathbf{F} into elastic and plastic parts, \mathbf{F}^e and \mathbf{F}^p (Kroner, 1960; Lee, 1969). Unfortunately, in their formulation the foregoing authors make the a priori assumption that \mathbf{F}^e be symmetric, an assumption that rules out a simple prescription for rotating the body rigidly and consequently is compatible with frame-indifference only with non-standard transformation rules that confuse frame-indifference with material symmetry;³ for that reason we do not use this hypothesis in the development of our theory.

A key feature controlling the *initial* plastic deformation of amorphous materials is known to be the evolution of the local free-volume associated with certain metastable states, and it is commonly believed that for glassy polymers the evolution of this free-volume is the major reason for the highly non-linear stress–strain behavior that precedes the yield-peak and gives rise to post-yield strain softening. Metallic glasses also show a “yield-drop” specially at high temperatures (e.g. Hey et al., 1998). In our theory, we represent this local free-volume by an internal-state variable η .⁴

An important feature of our theory is the assumption that the (Helmholtz) free energy depends on \mathbf{F}^p , an assumption that leads directly to a *backstress* in the underlying flow rule (cf. Gurtin, 2000, 2003). Physical arguments in support of an energetically induced backstress are given by Boyce and co-workers (e.g. Boyce et al., 1988; Arruda and Boyce, 1993b). But if energetic considerations are to play a major role, then it would seem appropriate to develop the theory within a framework that accounts for the first two laws of thermodynamics. For isothermal processes the first two laws typically collapse into a single dissipation inequality asserting that temporal changes in free energy be not greater than the rate at which work is performed. This dissipation inequality plays a fundamental role in our discussion of suitable constitutive equations.

Our development of the theory carefully accounts for restrictions placed on constitutive assumptions by frame-indifference and by a new mathematical definition of an amorphous material based on the notion that the constitutive relations for such materials should be invariant under all rotations of the reference configuration and, independently, all rotations of the relaxed configuration.

The plan of this paper is as follows. We develop the general theory in Sections 2–6. In Sections 7 and 8 we specialize our constitutive equations, and in Section 9 we summarize a set of specialized constitutive

² We use the words plastic and inelastic interchangeably, and emphasize that the micromechanisms leading to such deformations in amorphous solids are not related to dislocation-based micromechanisms that characterize the plastic deformation of crystalline metals. See Argon (1993) for a review on the micromechanisms of plastic deformation of amorphous solids. For a review of the physics of glassy polymers see Haward (1973) and Haward and Young (1997). For some recent reviews on aspects of bulk metallic glasses see Johnson (1999) and Inoue (2000).

³ Under a change in frame with rotation $\mathbf{Q} = \mathbf{Q}(t)$, the standard transformation rule transforms \mathbf{F}^e to $\mathbf{Q}\mathbf{F}^e$, but \mathbf{F}^e symmetric would not generally render $\mathbf{Q}\mathbf{F}^e$ symmetric. To accomodate this difficulty it is necessary to have \mathbf{F}^e transform to $\mathbf{Q}\mathbf{F}^e\mathbf{Q}^T$ and \mathbf{F}^p to $\mathbf{Q}\mathbf{F}^p$, a hypothesis that renders any relation between the Cauchy stress and \mathbf{F}^e isotropic.

⁴ The material itself is presumed to be plastically incompressible. We believe that because of the disparate difference between the scale of the macroscopic deformation and the scale of the local free-volume, the latter is better represented by an internal-state variable rather than by $J^p = \det \mathbf{F}^p$. In fact, in a previous version of this work we used J^p rather than η ; the final equations were far more complicated, but order-of-magnitude calculations as well as numerical calculations for polycarbonate lead us to believe that the predictions of the two theories would differ little.

equations that should be useful in applications. In Section 10, we apply the specialized equations to model the large-deformation response of the amorphous polymeric solid, polycarbonate, at ambient temperature and pressure. Finally, Section 11 contains concluding remarks.

2. Kinematics

2.1. Basic kinematics

We consider a homogeneous body B_R identified with the region of space it occupies in a fixed *reference configuration*, and denote by \mathbf{X} an arbitrary material point of B_R . A *motion* of B_R is then a smooth one-to-one mapping $\mathbf{x} = \mathbf{y}(\mathbf{X}, t)$ with *deformation gradient*, *velocity*, and *velocity gradient* given by⁵

$$\mathbf{F} = \nabla \mathbf{y}, \quad \mathbf{v} = \dot{\mathbf{y}}, \quad \mathbf{L} = \text{grad} \mathbf{v} = \dot{\mathbf{F}} \mathbf{F}^{-1}. \quad (2.1)$$

We base the theory on the Kröner–Lee decomposition (Kroner, 1960; Lee, 1969)

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p. \quad (2.2)$$

Here, suppressing the argument t :

- (i) $\mathbf{F}^p(\mathbf{X})$ represents the local deformation of *referential segments* $d\mathbf{X}$ to segments $d\mathbf{l} = \mathbf{F}^p(\mathbf{X})d\mathbf{X}$ in the *relaxed configuration* due to “plastic mechanisms”, such as the stretching, rotation, and relative slippage of the molecular chains in polymeric glasses, or the cumulative effects of inelastic transformations resulting from the cooperative action of atomic clusters in metallic glasses.
- (ii) $\mathbf{F}^e(\mathbf{X})$ represents the mapping of segments $d\mathbf{l}$ in the relaxed configuration into segments $d\mathbf{x} = \mathbf{F}^e(\mathbf{X})d\mathbf{l}$ in the *deformed configuration* due to “elastic mechanisms”, such as stretching and rotation of the intermolecular structure in polymeric glasses or the interatomic structure in metallic glasses.

The relaxed configuration might therefore be viewed as the ambient space into which an infinitesimal neighborhood of \mathbf{X} is carried by the linear transformation $\mathbf{F}^p(\mathbf{X})$ —or into which an infinitesimal neighborhood of $\mathbf{x} = \mathbf{y}(\mathbf{X})$ is pulled back by the transformation $\mathbf{F}^e(\mathbf{X})^{-1}$. We refer to \mathbf{F}^p and \mathbf{F}^e as the *plastic and elastic parts* of \mathbf{F} .

By (2.1) and (2.2),

$$\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e^{-1}}, \quad (2.3)$$

with

$$\mathbf{L}^e = \dot{\mathbf{F}}^e \mathbf{F}^{e^{-1}}, \quad \mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p^{-1}}. \quad (2.4)$$

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

$$\left. \begin{aligned} \mathbf{D}^e &= \text{sym} \mathbf{L}^e, & \mathbf{W}^e &= \text{skw} \mathbf{L}^e, \\ \mathbf{D}^p &= \text{sym} \mathbf{L}^p, & \mathbf{W}^p &= \text{skw} \mathbf{L}^p, \end{aligned} \right\} \quad (2.5)$$

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

⁵ Notation: ∇ 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 $\mathbf{x} = \mathbf{y}(\mathbf{X}, t)$ in the deformed configuration; a superposed dot denotes the material time-derivative. Throughout, we write $\mathbf{F}^{e^{-1}} = (\mathbf{F}^e)^{-1}$, $\mathbf{F}^{p^{-T}} = (\mathbf{F}^p)^{-T}$, etc. We write $\text{sym} \mathbf{A}$, $\text{skw} \mathbf{A}$, \mathbf{A}_0 , and $\text{sym}_0 \mathbf{A}$ respectively, for the 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 $\mathbf{A} \cdot \mathbf{B}$, and the magnitude of \mathbf{A} by $|\mathbf{A}| = \sqrt{\mathbf{A} \cdot \mathbf{A}}$.

2.2. Incompressible, irrotational plastic flow

We make two basic kinematical assumptions concerning plastic flow. Firstly, we make the standard assumption that the *flow is incompressible*, so that

$$\det \mathbf{F}^p = 1 \quad (2.6)$$

and

$$\text{tr } \mathbf{L}^p = 0.$$

Secondly, we assume that the *flow is irrotational* in the sense that⁶

$$\mathbf{W}^p = \mathbf{0}. \quad (2.7)$$

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

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p, \quad (2.8)$$

with \mathbf{D}^p *deviatoric*.

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

$$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e = \mathbf{V}^e \mathbf{R}^e, \quad \mathbf{F}^p = \mathbf{R}^p \mathbf{U}^p = \mathbf{V}^p \mathbf{R}^p, \quad (2.9)$$

where \mathbf{R}^e and \mathbf{R}^p are rotations, while \mathbf{U}^e , \mathbf{V}^e , \mathbf{U}^p , and \mathbf{V}^p are symmetric, positive-definite tensors. By (2.4), (2.7), and (2.9),

$$\dot{\mathbf{R}}^{p^T} \mathbf{R}^p = \text{skw}(\dot{\mathbf{U}}^p \mathbf{U}^{p^{-1}});$$

thus note that although $\mathbf{W}^p = \mathbf{0}$, the rotation \mathbf{R}^p need not be the identity.

We write

$$J = \det \mathbf{F} = \det \mathbf{F}^e. \quad (2.10)$$

2.3. 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

$$\mathbf{y}(\mathbf{X}, t) \rightarrow \mathbf{Q}(t) \mathbf{y}(\mathbf{X}, t) + \mathbf{q}(t), \quad (2.11)$$

with $\mathbf{Q}(t)$ a rotation (proper-orthogonal tensor) and $\mathbf{q}(t)$ a vector at each t . Thus

$$\mathbf{F} \rightarrow \mathbf{Q} \mathbf{F}. \quad (2.12)$$

The reference and relaxed configurations are independent of the choice of such changes in frame; thus the fields \mathbf{F}^p and \mathbf{D}^p are invariant under transformations of the form (2.11). This observation, (2.2) and (2.12) yield the transformation law

$$\mathbf{F}^e \rightarrow \mathbf{Q} \mathbf{F}^e, \quad (2.13)$$

so that $\mathbf{L}^e \rightarrow \mathbf{Q} \mathbf{L}^e \mathbf{Q}^T + \dot{\mathbf{Q}} \mathbf{Q}^T$ and hence

$$\mathbf{D}^e \rightarrow \mathbf{Q} \mathbf{D}^e \mathbf{Q}^T, \quad \mathbf{W}^e \rightarrow \mathbf{Q} \mathbf{W}^e \mathbf{Q}^T + \dot{\mathbf{Q}} \mathbf{Q}^T. \quad (2.14)$$

⁶ In Appendix B we give a formal argument, based on isotropy, showing that \mathbf{W}^p is orders of magnitude smaller than the elastic strains, granted they themselves are small.

3. Principle of virtual power: Macroscopic and microscopic force balances

The theory presented here is based on the belief that the power expended by each independent “rate-like” kinematical descriptor be expressible in terms of an associated force system consistent with its own balance. But the basic “rate-like” descriptors, namely, \mathbf{v} , \mathbf{L}^e , and \mathbf{D}^p are not independent, as they are constrained by (2.3), and it is not apparent what forms the associated force balances should take. For that reason, we determine these balances using the principle of virtual power.

We write B_R for the undeformed body and $B(t) = \mathbf{y}(B_R, t)$ for the *deformed body*. We use the term *part* to denote an arbitrary time-dependent subregion $P(t)$ of $B(t)$ that *deforms* with the body, so that

$$P(t) = \mathbf{y}(P_R, t) \quad (3.1)$$

for some *fixed* subregion P_R of B_R .

In what follows it is most convenient to label material points by their positions $\mathbf{x} = \mathbf{y}(\mathbf{X}, t)$ in the deformed configuration.

3.1. Principle of virtual power

Assume that, at some arbitrarily chosen but *fixed time*, the fields \mathbf{y} , \mathbf{F}^e , and (hence) \mathbf{F}^p are known, and consider the fields \mathbf{v} , \mathbf{L}^e , and \mathbf{D}^p as virtual velocities to be specified independently in a manner consistent with (2.3); that is, denoting the virtual fields by $\tilde{\mathbf{v}}$, $\tilde{\mathbf{L}}^e$, and $\tilde{\mathbf{D}}^p$ to differentiate them from fields associated with the actual evolution of the body, we require that

$$\text{grad } \tilde{\mathbf{v}} = \tilde{\mathbf{L}}^e + \mathbf{F}^e \tilde{\mathbf{D}}^p \mathbf{F}^{e^{-1}}. \quad (3.2)$$

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

$$\mathcal{V} = (\tilde{\mathbf{v}}, \tilde{\mathbf{L}}^e, \tilde{\mathbf{D}}^p)$$

consistent with (3.2).

We assume that under a change in frame the fields comprising a generalized virtual velocity transform as their non-virtual counterparts; i.e., e.g.,

$$\tilde{\mathbf{L}}^e \rightarrow \mathbf{Q} \tilde{\mathbf{L}}^e \mathbf{Q}^T + \dot{\mathbf{Q}} \mathbf{Q}^T. \quad (3.3)$$

The principle of virtual power is the assertion that, given any part P , the (virtual) power expended on P by material or bodies exterior to P be equal to the virtual power expended within P . Let \mathbf{n} denote the outward unit normal to ∂P . The external expenditure of power, which is standard, consists of a *macroscopic surface traction* $\mathbf{t}(\mathbf{n})$ and a *macroscopic body force* \mathbf{f} , each of whose working accompanies the macroscopic motion of the body. (The body force \mathbf{f} is assumed to include inertial forces.) We therefore write the external power in the form

$$\mathcal{W}_{\text{ext}}(P, \mathcal{V}) = \int_{\partial P} \mathbf{t}(\mathbf{n}) \cdot \tilde{\mathbf{v}} \, da + \int_P \mathbf{f} \cdot \tilde{\mathbf{v}} \, dv, \quad (3.4)$$

with $\mathbf{t}(\mathbf{n})$ (for each unit vector \mathbf{n}) and \mathbf{f} defined over the body for all time.

We assume that (virtual) power is expended internally by a *stress* \mathbf{T} work conjugate to $\tilde{\mathbf{L}}^e$ and an *internal microstress* \mathbf{T}^p work conjugate to $\tilde{\mathbf{D}}^p$. We therefore write the internal power in the form

$$\mathcal{W}_{\text{int}}(P, \mathcal{V}) = \int_P (\mathbf{T} \cdot \tilde{\mathbf{L}}^e + J^{-1} \mathbf{T}^p \cdot \tilde{\mathbf{D}}^p) \, dv. \quad (3.5)$$

The term J^{-1} arises because the microstress-power $\mathbf{T}^p \cdot \tilde{\mathbf{D}}^p$ is measured per unit volume in the relaxed configuration, but the integration is carried out within the deformed body. Here \mathbf{T} and \mathbf{T}^p are defined over the body for all time. We assume that \mathbf{T}^p is *symmetric and deviatoric*, since $\tilde{\mathbf{D}}^p$ is symmetric and deviatoric.

The precise statement of the *principle of virtual power* consists of two basic requirements:

(V1) (Power Balance) Given any part P ,

$$\mathcal{W}_{\text{ext}}(P, \mathcal{V}) = \mathcal{W}_{\text{int}}(P, \mathcal{V}) \quad \text{for all generalized virtual velocities } \mathcal{V}. \quad (3.6)$$

(V2) (Frame-Indifference) Given any part P and any generalized virtual velocity \mathcal{V} ,

$$\mathcal{W}_{\text{int}}(P, \mathcal{V}) \quad \text{is invariant all changes in frame.} \quad (3.7)$$

3.2. Macroscopic force and moment balances: Microforce balances

To deduce the consequences of the principle of virtual power, assume that (V1) and (V2) are satisfied. In applying the virtual balance (3.6) we are at liberty to choose any \mathcal{V} consistent with the constraint (3.2). We consider first a generalized virtual velocity with $\tilde{\mathbf{D}}^p \equiv \mathbf{0}$, so that $\text{grad}\tilde{\mathbf{v}} = \tilde{\mathbf{L}}^e$. For this choice of \mathcal{V} , (V1) yields

$$\int_{\partial P} \mathbf{t}(\mathbf{n}) \cdot \tilde{\mathbf{v}} da + \int_P \mathbf{f} \cdot \tilde{\mathbf{v}} dv = \int_P \mathbf{T} \cdot \text{grad}\tilde{\mathbf{v}} dv,$$

and, using the divergence theorem,

$$\int_{\partial P} (\mathbf{t}(\mathbf{n}) - \mathbf{T}\mathbf{n}) \cdot \tilde{\mathbf{v}} da + \int_P (\text{div}\mathbf{T} + \mathbf{f}) \cdot \tilde{\mathbf{v}} dv = 0.$$

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

$$\mathbf{t}(\mathbf{n}) = \mathbf{T}\mathbf{n}, \quad (3.8)$$

and the local force balance

$$\text{div}\mathbf{T} + \mathbf{f} = \mathbf{0}. \quad (3.9)$$

Next, consider the internal power $\mathcal{W}_{\text{int}}(P, \mathcal{V})$ under an arbitrary change in frame. In the new frame P transforms rigidly to a region P^* , \mathcal{V} to a generalized virtual velocity \mathcal{V}^* , \mathbf{T} to \mathbf{T}^* and \mathbf{T}^p to \mathbf{T}^{p^*} ; (V2) therefore implies that $\mathcal{W}_{\text{int}}(P, \mathcal{V}) = \mathcal{W}_{\text{int}}^*(P^*, \mathcal{V}^*)$. If we transform the integral over P^* to an integral over P and use the relevant transformation laws for \mathcal{V}^* , we find that,

$$\mathcal{W}_{\text{int}}^*(P^*, \mathcal{V}^*) = \int_P \{(\mathbf{T}^* \cdot (\mathbf{Q}\tilde{\mathbf{L}}^e\mathbf{Q}^T + \dot{\mathbf{Q}}\mathbf{Q}^T) + J^{-1}\mathbf{T}^{p^*} \cdot \tilde{\mathbf{D}}^p) dv.$$

Since P , the change in frame, and the fields $\tilde{\mathbf{L}}^e$ and $\tilde{\mathbf{D}}^p$ are arbitrary, and since $\dot{\mathbf{Q}}\mathbf{Q}^T$ is an arbitrary skew tensor, we may use (3.7) to conclude that \mathbf{T} is symmetric,

$$\mathbf{T} = \mathbf{T}^T, \quad (3.10)$$

and transforms according to

$$\mathbf{T} \rightarrow \mathbf{Q}\mathbf{T}\mathbf{Q}^T, \quad (3.11)$$

while \mathbf{T}^p is invariant. Thus \mathbf{T} plays the role of the *Cauchy stress*, and (3.9) and (3.10) represent the *macroscopic force and moment balances*.

For convenience we define

$$\mathbf{S}_0 = \text{sym}_0(J\mathbf{F}^T \mathbf{T} \mathbf{F}^{T^{-1}}), \quad (3.12)$$

where $\text{sym}_0(\cdots)$ denotes the symmetric-deviatoric part of the tensor (\cdots) . We next choose $\tilde{\mathbf{v}} \equiv \mathbf{0}$. Then the external power vanishes identically, so that, by (V1), the internal power must also vanish. Moreover, by (3.2), $\tilde{\mathbf{L}}^e = -\mathbf{F}^e \tilde{\mathbf{D}}^p \mathbf{F}^{e^{-1}}$. Thus, since P is arbitrary,

$$\mathbf{T}^p \cdot \tilde{\mathbf{D}}^p = J(\mathbf{F}^{e^T} \mathbf{T} \mathbf{F}^{e^{-T}}) \cdot \tilde{\mathbf{D}}^p. \quad (3.13)$$

Since $\tilde{\mathbf{D}}^p$ is an arbitrary symmetric, deviatoric tensor field, we find that

$$\mathbf{S}_0 = \mathbf{T}^p, \quad (3.14)$$

which represents a *microforce balance*.

Finally, writing $\mathcal{W}_{\text{ext}}(P)$ and $\mathcal{W}_{\text{int}}(P)$ for the external and internal powers when the actual (non-virtual) fields are used, we find, using the symmetry of \mathbf{T} , that

$$\mathcal{W}_{\text{int}}(P) = \int_P (\mathbf{T} \cdot \mathbf{D}^e + J^{-1} \mathbf{T}^p \cdot \mathbf{D}^p) dv. \quad (3.15)$$

4. Dissipation inequality (second law)

We consider a purely mechanical theory based on a second law requiring that the temporal increase in free energy of any part P be less than or equal to the power expended on P . Let ψ denote the *free energy*, measured per unit volume in the relaxed configuration. The second law therefore takes the form of a *dissipation inequality*

$$\overline{\int_P \dot{\psi} J^{-1} dv} \leq \mathcal{W}_{\text{ext}}(P) = \mathcal{W}_{\text{int}}(P). \quad (4.1)$$

Since $J^{-1} dv$ with $J = \det \mathbf{F}$ represents the volume measure in the reference configuration, and since $P = P(t)$ deforms with the body,

$$\overline{\int_P \dot{\psi} J^{-1} dv} = \int_P \dot{\psi} J^{-1} dv.$$

Thus, since P is arbitrary, we may use (3.15) to localize (4.1); the result is the *local dissipation inequality*

$$\dot{\psi} - J \mathbf{T} \cdot \mathbf{D}^e - \mathbf{T}^p \cdot \mathbf{D}^p \leq 0, \quad (4.2)$$

which will form a basis for our development of a suitable constitutive theory.

5. Constitutive theory

5.1. Constitutive equations

We introduce a list of n scalar *internal state-variables* $\xi = (\xi^1, \xi^2, \dots, \xi^n)$, and assume that

$$\left. \begin{aligned} \psi &= \hat{\psi}(\mathbf{F}^e, \mathbf{F}^p), \\ \mathbf{T} &= \hat{\mathbf{T}}(\mathbf{F}^e, \mathbf{F}^p), \\ \mathbf{T}^p &= \hat{\mathbf{T}}^p(\mathbf{F}^e, \mathbf{F}^p, \mathbf{D}^p, \xi), \\ \dot{\xi}^i &= h^i(\mathbf{F}^e, \mathbf{F}^p, \mathbf{D}^p, \xi). \end{aligned} \right\} \quad (5.1)$$

Note that we neglect from the outset rate-dependence in the elastic response of the material.

Under a change in frame \mathbf{F}^p and \mathbf{D}^p are invariant, while $\mathbf{F}^e \rightarrow \mathbf{Q}\mathbf{F}^e$; thus, using a standard argument, we see that frame-indifference reduces (5.1) to the specific form

$$\left. \begin{array}{l} \psi = \hat{\psi}(\mathbf{U}^e, \mathbf{F}^p), \\ \mathbf{T} = \mathbf{R}^e \hat{\mathbf{T}}(\mathbf{U}^e, \mathbf{F}^p) \mathbf{R}^{eT}, \\ \mathbf{T}^p = \hat{\mathbf{T}}^p(\mathbf{U}^e, \mathbf{F}^p, \mathbf{D}^p, \xi), \\ \dot{\xi}^i = h^i(\mathbf{U}^e, \mathbf{F}^p, \mathbf{D}^p, \xi). \end{array} \right\} \quad (5.2)$$

The following definitions help to make precise our notion of an amorphous material:

- (i) Orth^+ = the group of all rotations (the proper orthogonal group);
- (ii) the *referential symmetry group* G^{ref} is the group of all rotations of the *reference configuration* that leave the response of the material unaltered;
- (iii) the *relaxed symmetry group* G^{rel} is the group of all rotations of the *relaxed configuration* that leave the response of the material unaltered.

We refer to the material as amorphous (and to the reference and relaxed configurations as undistorted) if

$$G^{\text{ref}} = \text{Orth}^+, \quad G^{\text{rel}} = \text{Orth}^+, \quad (5.3)$$

so that the response of the material is invariant under arbitrary rotations of the reference and relaxed configurations.⁷

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 (3.15), or equivalently, the requirement that

$$\mathbf{T}^p \cdot \mathbf{D}^p \quad \text{and} \quad \mathbf{T} \cdot \mathbf{D}^e \text{ be invariant.} \quad (5.4)$$

Let \mathbf{Q} be a *rotation of the reference configuration*. Then

$$\mathbf{F}^p \rightarrow \mathbf{F}^p \mathbf{Q} \quad \text{and} \quad \mathbf{F}^e \text{ is invariant,} \quad (5.5)$$

so that, by (2.3), \mathbf{L}^e and \mathbf{D}^p and (hence) \mathbf{D}^e , and \mathbf{D}^p are invariant. We may therefore use (5.4) to conclude that \mathbf{T} and \mathbf{T}^p are invariant.

On the other hand, let \mathbf{Q} be a *rotation of the relaxed configuration*. Then

$$\mathbf{F}^p \rightarrow \mathbf{Q}^T \mathbf{F}^p \quad \text{and} \quad \mathbf{F}^e \rightarrow \mathbf{F}^e \mathbf{Q}, \quad (5.6)$$

and hence (2.3) yields the transformation law $\mathbf{D}^p \rightarrow \mathbf{Q}^T \mathbf{D}^p \mathbf{Q}$ and the invariance of \mathbf{L}^e , so that \mathbf{D}^e is invariant. Finally, (5.4) yields the invariance of \mathbf{T} and the transformation law $\mathbf{T}^p \rightarrow \mathbf{Q}^T \mathbf{T}^p \mathbf{Q}$.

We henceforth restrict attention to materials that are amorphous in the sense that the constitutive relations (5.1) (or equivalently, (5.2)) are invariant under all rotations of the reference configuration and, independently, all rotations of the relaxed configuration.

Applying the former with $\mathbf{Q} = \mathbf{R}^{pT}$ reduces (5.2) to

$$\left. \begin{array}{l} \psi = \hat{\psi}(\mathbf{U}^e, \mathbf{V}^p), \\ \mathbf{T} = \mathbf{R}^e \hat{\mathbf{T}}(\mathbf{U}^e, \mathbf{V}^p) \mathbf{R}^{eT}, \\ \mathbf{T}^p = \hat{\mathbf{T}}^p(\mathbf{U}^e, \mathbf{V}^p, \mathbf{D}^p, \xi), \\ \dot{\xi}^i = h^i(\mathbf{U}^e, \mathbf{V}^p, \mathbf{D}^p, \xi). \end{array} \right\} \quad (5.7)$$

⁷ For metallic and polymer glasses this notion attempts to characterize situations in which the material has a completely disordered atomic or molecular structure.

Let

$$\mathbf{C}^e = \mathbf{F}^{e^T} \mathbf{F}^e = (\mathbf{U}^e)^2, \quad \mathbf{B}^p = \mathbf{F}^p \mathbf{F}^{p^T} = (\mathbf{V}^p)^2,$$

and, in (5.7), replace \mathbf{R}^e by $\mathbf{F}^e \mathbf{U}^{e^{-1}}$, \mathbf{U}^e by $\sqrt{\mathbf{C}^e}$, and \mathbf{V}^p by $\sqrt{\mathbf{B}^p}$; this reduces (5.7) to

$$\left. \begin{aligned} \psi &= \bar{\psi}(\mathbf{C}^e, \mathbf{B}^p), \\ \mathbf{T} &= \mathbf{F}^e \bar{\mathbf{T}}(\mathbf{C}^e, \mathbf{B}^p) \mathbf{F}^{e^T}, \\ \mathbf{T}^p &= \bar{\mathbf{T}}^p(\boldsymbol{\Theta}), \\ \dot{\xi}^i &= h^i(\boldsymbol{\Theta}), \end{aligned} \right\} \quad (5.8)$$

where $\boldsymbol{\Theta}$ denotes the argument list

$$\boldsymbol{\Theta} = (\mathbf{C}^e, \mathbf{B}^p, \mathbf{D}^p, \boldsymbol{\xi}).$$

Our final step is to consider invariance under rotations of the relaxed configuration using the transformation rules specified in the paragraph containing (5.6). Under a rotation \mathbf{Q} of the relaxed configuration,

$$\mathbf{C}^e \rightarrow \mathbf{Q}^T \mathbf{C}^e \mathbf{Q}, \quad \mathbf{B}^p \rightarrow \mathbf{Q}^T \mathbf{B}^p \mathbf{Q},$$

and the response functions $\bar{\psi}$, $\bar{\mathbf{T}}$, $\bar{\mathbf{T}}^p$, and h^i appearing in (5.8) must each be *isotropic*.

5.2. Thermodynamic restrictions

With a view toward determining the restrictions imposed by the local dissipation inequality, note that

$$\dot{\psi} = \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \cdot \dot{\mathbf{C}}^e + \frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \cdot \dot{\mathbf{B}}^p.$$

Further, using the symmetry of $\partial \bar{\psi} / \partial \mathbf{C}^e$,

$$\frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \cdot \dot{\mathbf{C}}^e = \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \cdot (2\mathbf{F}^{e^T} \dot{\mathbf{F}}^e) = \left(2\mathbf{F}^e \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \mathbf{F}^{e^T} \right) \cdot \mathbf{L}^e = \left(2\mathbf{F}^e \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \mathbf{F}^{e^T} \right) \cdot \mathbf{D}^e$$

and similarly, since \mathbf{D}^p is symmetric, deviatoric,

$$\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \cdot \dot{\mathbf{B}}^p = \frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \cdot (2\dot{\mathbf{F}}^p \mathbf{F}^{p^T}) = \left(2 \frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) \cdot \mathbf{D}^p = 2 \text{sym}_0 \left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) \cdot \mathbf{D}^p.$$

Thus

$$\dot{\psi} = \left(2\mathbf{F}^e \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \mathbf{F}^{e^T} \right) \cdot \mathbf{D}^e + 2 \text{sym}_0 \left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) \cdot \mathbf{D}^p. \quad (5.9)$$

If we substitute (5.8) and (5.9) into the local dissipation inequality (4.2), we find that

$$\left\{ \mathbf{F}^e \left(2 \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} - J\bar{\mathbf{T}}(\mathbf{C}^e, \mathbf{B}^p) \right) \mathbf{F}^{e^T} \right\} \cdot \mathbf{D}^e + \left\{ 2 \text{sym}_0 \left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) - \bar{\mathbf{T}}^p(\mathbf{C}^e, \mathbf{B}^p, \mathbf{D}^p, \boldsymbol{\xi}) \right\} \cdot \mathbf{D}^p \leq 0. \quad (5.10)$$

This inequality is to hold for all values of \mathbf{C}^e , \mathbf{B}^p , $\boldsymbol{\xi}$, \mathbf{D}^e , and \mathbf{D}^p . Since \mathbf{D}^e appears linearly, its “coefficient” must vanish; thus $J\bar{\mathbf{T}} = 2\partial \bar{\psi} / \partial \mathbf{C}^e$. Thus, defining $\mathbf{Y}^p(\boldsymbol{\Theta})$ to be the difference $\bar{\mathbf{T}}^p(\boldsymbol{\Theta}) - 2 \text{sym}_0((\partial \bar{\psi} / \partial \mathbf{B}^p) \mathbf{B}^p)$, we are led to the following constitutive relations for the stresses:

$$\left. \begin{aligned} \mathbf{T} &= 2J^{-1}\mathbf{F}^e \left(\frac{\partial \bar{\psi}(\mathbf{C}^e, \mathbf{B}^p)}{\partial \mathbf{C}^e} \right) \mathbf{F}^{e^T}, \\ \mathbf{T}^p &= 2\text{sym}_0 \left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) + \mathbf{Y}^p(\boldsymbol{\Theta}), \end{aligned} \right\} \quad (5.11)$$

where the response function \mathbf{Y}^p must satisfy

$$\mathbf{Y}^p(\boldsymbol{\Theta}) \cdot \mathbf{D}^p \geq 0. \quad (5.12)$$

The left side of (5.12) represents the *energy dissipated*, measured per unit volume in the relaxed configuration. To rule out trivial special cases, we assume that the material is *strictly dissipative* in the sense that

$$\mathbf{Y}^p(\boldsymbol{\Theta}) \cdot \mathbf{D}^p > 0 \quad \text{for } \mathbf{D}^p \neq \mathbf{0}. \quad (5.13)$$

6. Flow rule

We define

$$\mathbf{S}_{\text{back}} = 2\text{sym}_0 \left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p \right) \quad (6.1)$$

as a backstress. Then a central result of the theory—which follows upon using the constitutive relation (5.11)₂ and the microforce balance (3.14)—is the *flow rule*

$$\mathbf{S}_0 - \mathbf{S}_{\text{back}} = \mathbf{Y}^p(\boldsymbol{\Theta}). \quad (6.2)$$

In light of the dissipation inequality (5.12), we refer to $\mathbf{Y}^p(\boldsymbol{\Theta})$ as the *dissipative flow stress*.

It is convenient to write

$$\mathbf{T}^e = J\mathbf{F}^{e^{-1}}\mathbf{T}\mathbf{F}^{e^{-T}}. \quad (6.3)$$

Then, by (5.11)₁,

$$\mathbf{T}^e = 2 \frac{\partial \bar{\psi}(\mathbf{C}^e, \mathbf{B}^p)}{\partial \mathbf{C}^e}; \quad (6.4)$$

\mathbf{T}^e represents the Cauchy stress pulled back to the relaxed configuration. Then, by (3.12),

$$\mathbf{S}_0 = \text{sym}_0(\mathbf{C}^e \mathbf{T}^e), \quad (6.5)$$

and using (6.4),

$$\mathbf{S}_0 = 2\text{sym}_0 \left(\mathbf{C}^e \frac{\partial \bar{\psi}}{\partial \mathbf{C}^e} \right). \quad (6.6)$$

7. Specialization of the constitutive equations

The constitutive restrictions derived thus far are fairly general. With a view towards applications we now simplify the theory by imposing additional constitutive assumptions based on experience with existing theories of viscoplasticity and amorphous materials.

7.1. Free energy

To state the constitutive relation for the free energy it is convenient to define an *effective plastic stretch* by

$$\lambda^p = \frac{1}{\sqrt{3}} \sqrt{\text{tr } \mathbf{B}^p} = \frac{1}{\sqrt{3}} |\mathbf{V}^p|. \quad (7.1)$$

We consider a non-interactive free energy of the form

$$\bar{\psi}(\mathbf{C}^e, \mathbf{B}^p) = \psi^e(\mathbf{C}^e) + \psi^p(\mathbf{B}^p), \quad (7.2)$$

with

$$\left. \begin{aligned} \psi^e(\mathbf{C}^e) &\geq 0, & \psi^e(\mathbf{1}) &= 0, \\ \psi^p(\mathbf{B}^p) &\geq 0, & \psi^p(\mathbf{1}) &= 0. \end{aligned} \right\} \quad (7.3)$$

Then, by (6.4),

$$\mathbf{T}^e = 2 \frac{\partial \psi^e}{\partial \mathbf{C}^e}. \quad (7.4)$$

We assume further that the plastic energy has the specific form

$$\psi^p(\mathbf{B}^p) = \Psi(\lambda^p) \geq 0, \quad \Psi(1) = 0. \quad (7.5)$$

In view of (7.1),

$$\frac{\partial \psi^p}{\partial \mathbf{B}^p} = \frac{\mu}{2} \mathbf{1}, \quad \text{where } \mu = \frac{1}{3\lambda^p} \frac{\partial \Psi}{\partial \lambda^p}. \quad (7.6)$$

Thus, by (6.1), the symmetric and deviatoric backstress is given by

$$\mathbf{S}_{\text{back}} = \mu \mathbf{B}_0^p. \quad (7.7)$$

7.2. Dissipative flow stress. Inversion of the flow rule

It is convenient to write Λ for the list

$$\Lambda = (\mathbf{C}^e, \mathbf{B}^p, \xi).$$

We assume that the dissipative flow stress \mathbf{Y}^p has the specific form⁸

$$\mathbf{Y}^p(\boldsymbol{\theta}) = \ell(\Lambda) |\mathbf{D}^p|^{m-1} \mathbf{D}^p, \quad 0 < m \leq 1, \quad (7.8)$$

where

$$\ell(\Lambda) > 0 \quad (7.9)$$

to ensure satisfaction of the dissipation inequality (5.13). Here m is a constant; the limit $m \rightarrow 0$ renders (7.8) rate-independent, while $m = 1$ renders (7.8) linearly viscous.⁹

⁸ Thus the dissipative plastic stress \mathbf{Y}^p is parallel to—and points in the same direction as—the deviatoric plastic stretching tensor \mathbf{D}^p ; this corresponds to an assumption of “maximal dissipation” or an assumption of microstability (cf. Gurtin, 2003, Sections 5.2 and 5.3). In the rate-independent context, an analogous principle of maximum-dissipation has been variously attributed to R. von Mises, G.I. Taylor, and R. Hill (see Lubliner, 1990).

⁹ More elaborate forms for the rate-dependence may be considered, but a simple power-law rate-dependence makes the structure of our theory more transparent.

In view of (7.8), the flow rule (6.2) becomes

$$\mathbf{S}_0 - \mathbf{S}_{\text{back}} = \ell(\Lambda) |\mathbf{D}^p|^{m-1} \mathbf{D}^p. \quad (7.10)$$

The limit $m \rightarrow 0$ gives a standard Mises-type flow rule,

$$\mathbf{S}_0 - \mathbf{S}_{\text{back}} = \ell(\Lambda) \frac{\mathbf{D}^p}{|\mathbf{D}^p|}. \quad (7.11)$$

In this case $|\mathbf{S}_0 - \mathbf{S}_{\text{back}}| = \ell(\Lambda)$, which shows that $\ell(\Lambda)$ is the radius of a corresponding yield surface.

For $m > 0$ the flow rule (7.10) may be inverted. With this in mind, the following *inversion lemma* will be useful: Assume that $0 < m \leq 1$. Let $q > 0$ be given. Then the relation

$$\mathbf{A} = q |\mathbf{H}|^{m-1} \mathbf{H} \quad (7.12)$$

between tensors \mathbf{A} and \mathbf{H} is invertible with inverse

$$\mathbf{H} = k |\mathbf{A}|^{(1-m)/m} \mathbf{A}, \quad k = q^{-1/m}. \quad (7.13)$$

Indeed, taking the norm of both sides of (7.12) gives $|\mathbf{A}| = \ell |\mathbf{H}|^m$, and this, in turn, may be used to invert (7.12).

Using the inversion lemma and (7.10), we may rewrite the flow rule in the form

$$\mathbf{D}^p = k(\Lambda) |\mathbf{S}_0 - \mu \mathbf{B}_0^p|^{(1-m)/m} (\mathbf{S}_0 - \mu \mathbf{B}_0^p), \quad (7.14)$$

with

$$k(\Lambda) = \ell(\Lambda)^{-1/m}. \quad (7.15)$$

7.3. Internal variables

We restrict the list ξ of internal variables to two variables: a variable

$$s > 0$$

that represents the intermolecular resistance to plastic flow; and an unsigned variable η that represents the local free-volume.¹⁰ We assume that the evolution of these state variables (cf. (5.8)₄) is given by

$$\left. \begin{aligned} \dot{s} &= h(\Lambda, |\mathbf{D}^p|), \\ \dot{\eta} &= g(\Lambda, |\mathbf{D}^p|). \end{aligned} \right\} \quad (7.16)$$

8. Approximate theory for small elastic stretches

As our goal is a theory involving “small” elastic stretches, we introduce the *elastic strain*

$$\mathbf{E}^e = \frac{1}{2} (\mathbf{C}^e - \mathbf{1}). \quad (8.1)$$

Moreover, we restrict attention to the classical elastic strain-energy

$$\psi^e(\mathbf{C}^e) = G |\mathbf{E}_0^e|^2 + \frac{1}{2} K |\text{tr} \mathbf{E}^e|^2, \quad (8.2)$$

¹⁰ A key feature controlling the initial plastic deformation of amorphous materials is known to be the evolution of the local free-volume associated with the metastable state of these materials. It is commonly believed that the evolution of the local free-volume is the major reason for the highly non-linear stress-strain behavior of glassy materials (amorphous polymers at ambient temperatures, and amorphous metals at high temperatures) which precedes the yield-peak and gives rise to the post-yield strain-softening.

where G and K are the elastic shear and bulk moduli. By (7.4) and (8.1), the stress–strain relation corresponding to the strain energy (8.2), decomposed into deviatoric and spherical parts, then becomes

$$\mathbf{T}_0^e = 2G\mathbf{E}_0^e, \quad \text{tr } \mathbf{T}^e = 3K\text{tr } \mathbf{E}^e. \quad (8.3)$$

We assume henceforth that the elastic stretches are small in the sense that

$$\mathbf{U}^e \approx \mathbf{1}.$$

Then, since $J\mathbf{F}^{e^{-1}}\mathbf{T}\mathbf{F}^{e^{-T}} \approx \mathbf{R}^{e^T}\mathbf{T}\mathbf{R}^e$, we may use (6.3) and (6.5) to conclude that

$$\mathbf{T}^e \approx \mathbf{R}^{e^T}\mathbf{T}\mathbf{R}^e, \quad \mathbf{S}_0 \approx \mathbf{T}_0^e, \quad -\frac{1}{3}\text{tr } \mathbf{T}^e \approx \pi, \quad (8.4)$$

where π is the *mean normal pressure*

$$\pi = -\frac{1}{3}\text{tr } \mathbf{T}. \quad (8.5)$$

As a further simplification of the theory, we assume that the constitutive moduli k , h , and g depend on the list $\Lambda = (\mathbf{C}^e, \mathbf{B}^p, \xi)$ through dependences on $\text{tr } \mathbf{E}^e$, λ^p , η , and s , or, since $\pi \approx -K \text{tr } \mathbf{E}^e$, through dependences on π , λ^p , η , and s . We therefore write the flow rule in the form

$$\mathbf{T}_0^e - \mu\mathbf{B}_0^p = \ell(\pi, \lambda^p, \eta, s)|\mathbf{D}^p|^{m-1}\mathbf{D}^p, \quad (8.6)$$

with inverse

$$\mathbf{D}^p = k(\pi, \lambda^p, \eta, s)|\mathbf{T}_0^e - \mu\mathbf{B}_0^p|^{(1-m)/m}(\mathbf{T}_0^e - \mu\mathbf{B}_0^p), \quad k = \ell^{-1/m}. \quad (8.7)$$

Note that \mathbf{D}^p is parallel to—and points in the same direction as—the tensor-difference $\mathbf{T}_0^e - \mu\mathbf{B}_0^p$.

Similarly, the differential equations (7.16) now have $\Lambda = (\pi, \lambda^p, \eta, s)$.

9. Final constitutive equations assuming small elastic stretches and an initial virgin state

In terms of the variables

$\mathbf{T}, \mathbf{T} = \mathbf{T}^T$,	Cauchy stress,
$\mathbf{F}, \det \mathbf{F} > 0$,	deformation gradient,
$\mathbf{F}^p, \det \mathbf{F}^p = 1$,	plastic part of the deformation gradient,
$s, s > 0$,	isotropic resistance to plastic flow,
η ,	free volume,

and the definitions

$\mathbf{F}^e = \mathbf{F}\mathbf{F}^{p^{-1}}, \det \mathbf{F}^e > 0$,	elastic deformation gradient,
$\mathbf{C}^e = \mathbf{F}^{e^T}\mathbf{F}^e$,	elastic right Cauchy–Green strain,
$\mathbf{E}^e = \frac{1}{2}(\mathbf{C}^e - \mathbf{1})$,	elastic strain,
$\mathbf{T}^e = \mathbf{R}^{e^T}\mathbf{T}\mathbf{R}^e$,	stress conjugate to the elastic strain \mathbf{E}^e ,
$\pi = -\frac{1}{3}\text{tr } \mathbf{T}$,	mean normal pressure,
$\mathbf{T}_0^e = \mathbf{T}^e + \pi\mathbf{1}$,	deviatoric stress,
$\mathbf{B}^p = \mathbf{F}^p\mathbf{F}^{p^T}$,	left Cauchy–Green tensor corresponding to \mathbf{F}^p ,
$\mathbf{B}_0^p = \mathbf{B}^p - \frac{1}{3}(\text{tr } \mathbf{B}^p)\mathbf{1}$,	deviatoric part of \mathbf{B}^p ,
$\lambda^p = \frac{1}{\sqrt{3}}\sqrt{\text{tr } \mathbf{B}^p}$,	effective plastic stretch,

we summarize below a special set of constitutive equations that should be useful in applications:

1. *Free Energy*:

$$\psi = \psi^e + \psi^p, \quad (9.1)$$

$$\psi^e = G|\mathbf{E}_0^e|^2 + \frac{1}{2}K|\text{tr } \mathbf{E}^e|^2, \quad (9.2)$$

$$\psi^p = \Psi(\lambda^p) \geq 0, \quad \Psi(1) = 0. \quad (9.3)$$

Here G and K are the elastic shear and bulk moduli, respectively.

2. *Equation for the stress*:

$$\mathbf{T}^e = 2G\mathbf{E}_0^e + K(\text{tr } \mathbf{E}^e)\mathbf{1}. \quad (9.4)$$

3. *Flow rule*:

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

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p, \quad \mathbf{F}^p(\mathbf{X}, 0) = \mathbf{1}, \quad (9.5)$$

with \mathbf{D}^p given by the flow rule

$$\mathbf{D}^p = k(\pi, \lambda^p, \eta, s)|\mathbf{T}_0^e - \mu\mathbf{B}_0^p|^{(1-m)/m}(\mathbf{T}_0^e - \mu\mathbf{B}_0^p), \quad (9.6)$$

where

$$\mu = \frac{1}{3\lambda^p} \frac{\partial \Psi}{\partial \lambda^p}. \quad (9.7)$$

4. *Evolution equations for the internal variables s and η* :

$$\left. \begin{aligned} \dot{s} &= h(\pi, \lambda^p, \eta, s, |\mathbf{D}^p|), & s(\mathbf{X}, 0) &= s_0, \\ \dot{\eta} &= g(\pi, \lambda^p, \eta, s, |\mathbf{D}^p|), & \eta(\mathbf{X}, 0) &= 0, \end{aligned} \right\} \quad (9.8)$$

with s_0 a constitutive modulus that represents the initial resistance to flow. Here h , may take on positive (hardening) and negative (softening) values. Also, as is tacit from (9.8)₂, the free volume is measured from the value $\eta = 0$ in the virgin state of the material, and thus η at any other time represents a change in the free-volume from the initial state.

To complete the constitutive model for a particular amorphous material the constitutive parameter/functions that need to be specified are

$$\{G, K, \Psi, k, h, g, s_0\}.$$

10. Application to an amorphous polymeric solid

In this section we further specialize our constitutive model and apply it to describe the deformation response of the technologically important amorphous polymeric solid, polycarbonate, at atmospheric pressure and room temperature.¹¹

¹¹ The glass transition temperature for polycarbonate is ≈ 145 °C.

In amorphous polymeric materials the major part of ψ^p arises from an “entropic” contribution. Motivated by statistical mechanics models of rubber elasticity (cf. Treloar, 1975; Arruda and Boyce, 1993a; Anand, 1996) we consider two specific forms:

1. For small to moderate values of λ^p , we consider the simple *neo-Hookean* form

$$\psi^p = \mu \frac{3}{2} \{(\lambda^p)^2 - 1\}, \quad (10.1)$$

with μ a *constant* equal to the backstress modulus (9.7).

2. For larger values of λ^p , we consider the *Langevin-inverse* form

$$\psi^p = \mu_R \lambda_L^2 \left[\left(\frac{\lambda^p}{\lambda_L} \right) x + \ln \left(\frac{x}{\sinh x} \right) - \left(\frac{1}{\lambda_L} \right) y - \ln \left(\frac{y}{\sinh y} \right) \right], \quad (10.2)$$

$$x = \mathcal{L}^{-1} \left(\frac{\lambda^p}{\lambda_L} \right), \quad y = \mathcal{L}^{-1} \left(\frac{1}{\lambda_L} \right), \quad (10.3)$$

where \mathcal{L}^{-1} is the inverse¹² of the Langevin function $\mathcal{L}(\dots) = \coth(\dots) - (\dots)^{-1}$.

This functional form for ψ^p involves two material parameters: μ_R , called the *rubbery modulus*, and λ_L called the *network locking stretch*. In this case, from (9.7), the backstress modulus is

$$\mu = \mu_R \left(\frac{\lambda_L}{3\lambda^p} \right) \mathcal{L}^{-1} \left(\frac{\lambda^p}{\lambda_L} \right). \quad (10.4)$$

The modulus $\mu \rightarrow \infty$ as $\lambda^p \rightarrow \lambda_L$, since $\mathcal{L}^{-1}(z) \rightarrow \infty$ as $z \rightarrow 1$.

Graphs of ψ^p versus λ^p for representative values¹³ of material parameters for the neo-Hookean energy ($\mu = 16.95$ MPa), and for the form involving the inverse Langevin function ($\mu_R = 11$ MPa, $\lambda_L = 1.45$) are shown in Fig. 1a. The corresponding graphs for the backstress modulus μ are shown in Fig. 1b.

Next, to make connection with the existing literature, we introduce an it equivalent shear-stress and equivalent plastic shear-strain rate defined by

$$\bar{\tau} = \frac{1}{\sqrt{2}} |\mathbf{T}_0^e - \mu \mathbf{B}_0^p|, \quad v^p = \sqrt{2} |\mathbf{D}_0^p|, \quad (10.5)$$

respectively. Further, introducing two additional material parameters, v_0 , a reference plastic shear-strain rate, and α , a *pressure sensitivity parameter*, and writing C for the inconsequential constant $\sqrt{2}(\sqrt{2}/v_0)^m$, we set

$$\ell(\pi, \lambda^p, \eta, s) = C(s + \alpha\pi), \quad (10.6)$$

and recall that we require $\ell > 0$ to ensure satisfaction with the dissipation inequality (5.12). Then

$$\mathbf{D}^p = v^p \left(\frac{\mathbf{T}_0^e - \mu \mathbf{B}_0^p}{2\bar{\tau}} \right), \quad v^p = v_0 \left(\frac{\bar{\tau}}{s + \alpha\pi} \right)^{1/m}. \quad (10.7)$$

¹² To evaluate $x = \mathcal{L}^{-1}(y)$ for a given y in the range $0 < y < 1$, we numerically solve the non-linear equation $f(x) = \mathcal{L}(x) - y = 0$ for x .

¹³ These numbers are based on our estimates (to be discussed shortly) for polycarbonate.

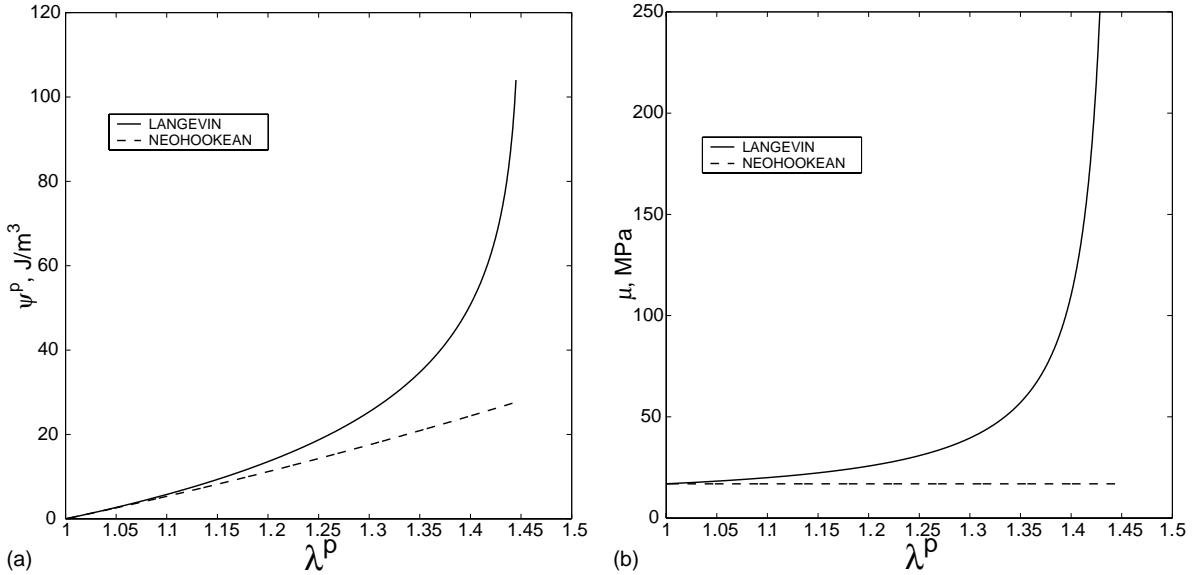


Fig. 1. (a) Comparison of the Langevin inverse and neo-Hookean forms of the plastic free energy ψ^p and (b) comparison of the corresponding forms for the backstress modulus μ .

We consider the evolution equations (9.8) in the special coupled rate-independent form ¹⁴

$$\left. \begin{aligned} \dot{s} &= h_0 \left(1 - \frac{s}{\tilde{s}(\eta)} \right) v^p, \\ \dot{\eta} &= g_0 \left(\frac{s}{s_{cv}} - 1 \right) v^p, \end{aligned} \right\} \quad (10.8)$$

with

$$\tilde{s}(\eta) = s_{cv}[1 + b(\eta_{cv} - \eta)], \quad (10.9)$$

where $\{h_0, g_0, s_{cv}, b, \eta_{cv}\}$ are additional material parameters. Here $\tilde{s} = \tilde{s}(\eta)$ is a saturation value of s : \dot{s} is positive for $s < \tilde{s}$ and negative for $s > \tilde{s}$. By definition v^p is non-negative. Assuming that $v^p > 0$, we may by a change in time scale transform (10.8) into a pair of ODEs. This system has a single equilibrium point (s_{cv}, η_{cv}) in the (s, η) -plane, and it is globally stable. Thus all solutions satisfy

$$s \rightarrow s_{cv} \quad \text{and} \quad \eta \rightarrow \eta_{cv} \quad \text{as } t \rightarrow \infty.$$

We restrict attention to the initial conditions $s = s_0$ and $\eta = 0$, with

$$s_0 \leq s \leq s_{cv}(1 + b\eta_{cv}).$$

Then a study of the phase portrait shows that η increases monotonically to its equilibrium value η_{cv} , while s increases monotonically to a peak and then decreases monotonically to its equilibrium value s_{cv} , thus capturing the observed yield-peak in the flow resistance.

¹⁴ We expect that \tilde{s} (and perhaps h_0 and g_0) may, in general, depend on v^p , but currently there is insufficient experimental evidence to warrant such a refinement.

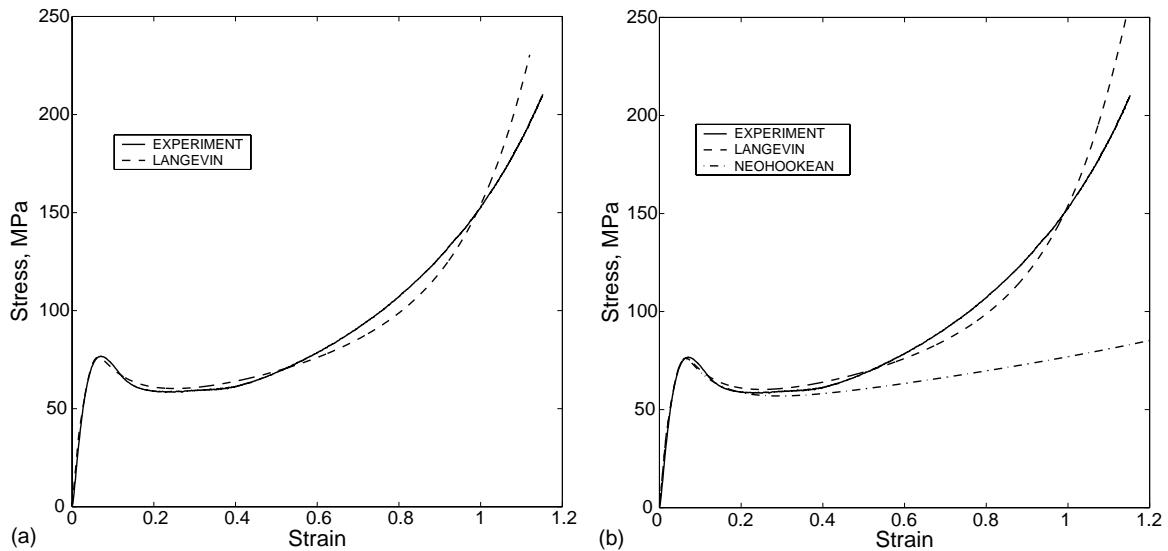


Fig. 2. (a) Stress–strain response of polycarbonate in simple compression, together with a fit of the constitutive model using the Langevin form for ψ^p and (b) comparison of the stress–strain responses calculated using the Langevin form and the neo-Hookean form for ψ^p .

We have implemented our constitutive model in the finite-element computer program ABAQUS/Explicit (ABAQUS, 2001) by writing a user material subroutine. Using this finite-element program, we next present results to some representative problems.

A stress–strain curve obtained from a monotonic simple compression experiment¹⁵ conducted at a constant logarithmic strain rate of -0.001 s^{-1} is shown in Fig. 2; absolute values of stress and strain are plotted. After an initial approximately linear region, the stress–strain curve becomes markedly non-linear prior to reaching a peak in the stress; the material then strain-softens to a quasi-plateau before beginning a broad region of rapid strain hardening.

We discuss below the results of our efforts at *estimation* of the material parameters for our constitutive model.¹⁶ Recall that the material parameters that need to be determined are

1. The elastic shear and bulk moduli (G, K) in the elastic part of the free energy.
2. The parameter μ in the neo-Hookean form, or the parameters (μ_R, λ_L) in the inverse Langevin form of the plastic free energy.
3. The parameters $\{v_0, m, \alpha, h_0, g_0, s_{cv}, b, \eta_{cv}, s_0\}$ in the flow rule and the evolution equations for (s, η) .

¹⁵ All experiments reported in this paper were performed by Mr. B.P. Gearing as part of his doctoral research at MIT. As is well known, the mechanical response of amorphous thermoplastics is very sensitive to prior thermo-mechanical processing history. The experiments were conducted on polycarbonate specimens which were annealed at the glass transition temperature of this material, 145 °C, for 2 h, and then furnace-cooled to room temperature in approximately 15 h. The experiments reported here were conducted under isothermal conditions at room temperature.

¹⁶ We have not attempted to carry out a comprehensive experimental program to obtain precise numbers for polycarbonate. The purpose of this section is to emphasize only the qualitative features of the theory. We leave a more detailed comparison of theory against experiment for future work.

The values of (G, K) are determined by measuring the Young's modulus and Poisson's ratio of the material in a compression experiment and using standard conversion relations of isotropic elasticity to obtain the elastic shear and bulk moduli. The parameters $\{v_0, m\}$ are estimated by conducting a strain rate jump experiment in simple compression, and the pressure sensitivity parameter α is estimated from compression experiments under superposed hydrostatic pressure reported in the literature. The parameters $\{h_0, g_0, s_{cv}, b, \eta_{cv}, s_0\}$ and (μ_R, λ_L) may be estimated by fitting a stress-strain curve in compression to large strains. Once (μ_R, λ_L) are estimated so as to fit the data for large strains, then the value of μ in the neo-Hookean form of ψ^P is easily obtained from (10.4) as the limit at $\lambda^P = 1$.

Using a value of $\alpha = 0.08$ from the data reported by Spitzig and Richmond (1979), a value of $v_0 = 0.0017 \text{ s}^{-1}$ and a strain rate-sensitivity parameter $m = 0.011$ obtained from a strain rate jump experiment, the parameters $\{G, K, \mu_R, \lambda_L, h_0, g_0, s_{cv}, b, \eta_{cv}, s_0\}$ were estimated by fitting the stress-strain curve for polycarbonate in simple compression (Fig. 2). The fit was performed by judiciously adjusting the values of these parameters in finite element simulations of a simple compression experiment (assuming homogeneous deformation) using a single ABAQUS/C3D8R element. After a few attempts, a reasonable fit was obtained, and this is shown in Fig. 2a. The list of parameters obtained using this heuristic calibration procedure are:¹⁷

$$\begin{aligned} G &= 0.857 \text{ GPa}, & K &= 2.24 \text{ GPa}, & \mu_R &= 11.0 \text{ MPa}, & \lambda_L &= 1.45, \\ v_0 &= 0.0017 \text{ s}^{-1}, & m &= 0.011, & \alpha &= 0.08, \\ h_0 &= 2.75 \text{ GPa}, & s_{cv} &= 24.0 \text{ MPa}, & b &= 825, & \eta_{cv} &= 0.001, \\ g_0 &= 6.0 \times 10^{-3}, & s_0 &= 20.0 \text{ MPa}. \end{aligned}$$

Fig. 2b shows a comparison of the stress-strain response calculated using the inverse Langevin form for ψ^P and the list of material parameters above, against the stress-strain response calculated using the neo-Hookean form for ψ^P with the same material parameters, except that the pair of constants (μ_R, λ_L) are replaced by the single constant $\mu = 16.95 \text{ MPa}$. This comparison shows that the simple neo-Hookean form for ψ^P may be adequate for applications involving logarithmic strains less than $\approx 35\%$. In the remaining part of our discussion we shall concentrate on the predictions of the model using the inverse Langevin form of ψ^P .

A representative stress-strain curve obtained from a simple compression experiment conducted to a strain level of ≈ -0.9 , and then unloaded to zero stress is shown in Fig. 3. The experiment clearly exhibits reverse yielding upon unloading due to the development of a backstress. A corresponding numerical calculation which exhibits the same response is also shown in Fig. 3. The numerical simulation was carried out using the material parameters determined by fitting the *monotonic compression experiment*, as discussed above; the unloading part of the stress-strain curve was not used to adjust the material parameters. The correspondence between the predicted unloading response from the model and the actual experiment is very encouraging.

Finally, Fig. 4a shows a representative experimentally measured load-displacement curve in a tension experiment on a specimen with a cylindrical gauge section. At the peak load a pronounced neck forms in the gauge section, the load subsequently decreases to an approximate plateau value, and the neck propagates along the gauge section. To numerically model this experiment, one half of a specimen was meshed with 390 ABAQUS/CAX4R axisymmetric elements. As before, the constitutive parameters used in the simulation are those obtained from the fitting exercise for the compression experiment. The calculated load-displacement response is also shown in Fig. 4a. Deformed geometries are shown in Fig. 4b and c at the two displacement levels which have been marked in Fig. 4a. The deformation is homogeneous until the peak load. Subsequent to the peak load, at location 1, a localized neck has formed at the center of the gauge

¹⁷ This list, although not unique, seems adequate for illustrative purposes.

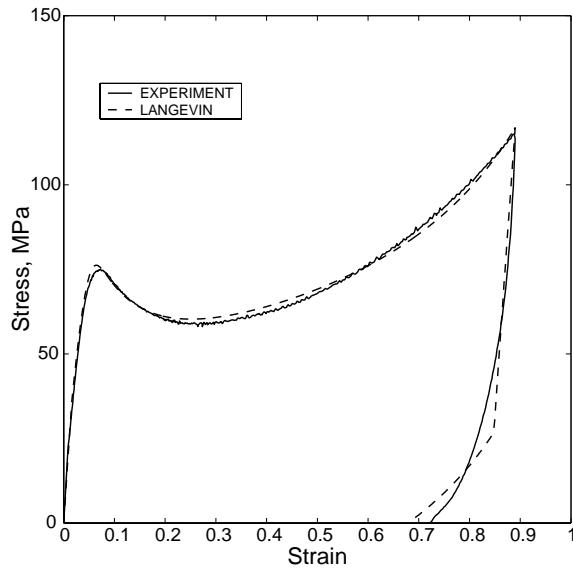


Fig. 3. Stress–strain response of polycarbonate in simple compression showing reverse yielding upon unloading due to the development of back stress. The calculated response shows the same phenomenon.

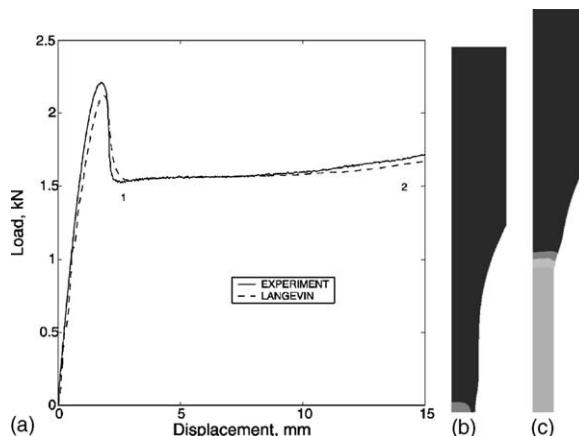


Fig. 4. (a) Experimental and numerical load–displacement curves in tension; two displacement levels of interest are marked. (b) Deformed geometry at displacement level 1 showing the beginnings of neck formation; (c) at displacement level 2 showing that the neck has propagated along the gauge section of the specimen.

section, and by stage 2 the neck has propagated along the gauge section, as was observed in the corresponding experiment.

11. Concluding remarks

We have shown an application of our theory to an amorphous polymeric solid in the previous section. Here the explicit dependence of the Helmholtz free energy on \mathbf{F}^p , led us directly to a resistance to plastic

flow as represented by the backstress, S_{back} . For amorphous metallic solids we expect that the dependence of the free energy on \mathbf{F}^p should be considerably smaller than that in amorphous polymers,¹⁸ and in this case we expect that our constitutive model should also be applicable, provided the backstress in the model is neglected.¹⁹

The current generation of bulk metallic glasses are believed to have many potential applications resulting from their unique properties: superior strength (≈ 1.8 GPa), and high yield strain ($\approx 2\%$); thus the elastic strain energy that can be stored in these materials is extremely high (e.g., Johnson, 1999; Inoue, 2000). However, when a metallic glass is deformed at ambient temperatures the plastic deformation is inhomogeneous, and is characterized by the formation of intense localized shear bands;²⁰ fracture typically occurs after very small inelastic strain in tension, and an inelastic strain of only a few percent in compression. In contrast, these materials exhibit a high strain-rate sensitivity (large value of m), and large inelastic strains at temperatures greater than approximately 70% of the glass transition temperature of the material. This opens the possibility of using conventional metal forming technologies to manufacture structural components from this relatively new class of materials. Thus there is growing interest in studying the large deformation response of bulk metallic glasses in this high temperature range (e.g. Nieh et al., 2001). We believe that our constitutive model, when suitably calibrated, might be useful for such applications.

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Appendix A. Texture induced by plastic deformation; initial texture

Consider a process in which the material in the neighborhood of an arbitrary material point \mathbf{X} is first loaded and then unloaded to a state in which $\mathbf{F}^e = \mathbf{1}$. The resulting residual plastic distortion \mathbf{F}^p at \mathbf{X} would then have an associated texture with directional characteristics represented by the principal directions of the strain tensor \mathbf{V}^p and texture strength by the associated principal stretches. Generally one would consider processes starting from the virgin state of the body, so that $\mathbf{F}^p(\mathbf{X}, 0) = \mathbf{1}$. But our theory does not rule out the possibility of starting at a plastically deformed state in the sense that²¹

$$\mathbf{F}^p(\mathbf{X}, 0) \neq \mathbf{1}.$$

In this case the material would possess *initial texture* defined by the initial strain tensor $\mathbf{V}^p(\mathbf{X}, 0)$. Moreover, since neither the flow rule (6.2) nor the constitutive equations (5.8) exhibit dependences on \mathbf{R}^p , and since the evolution equation $\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p$ for \mathbf{F}^p is invariant under any transformation of the form $\mathbf{F}^p \rightarrow \mathbf{F}^p \mathbf{H}$ with

¹⁸ The two-dimensional molecular dynamic simulations of the deformation of an atomic glass of Deng et al. (1989) do show the development of a Bauschinger effect (their Fig. 8). However, we have not found a report of the Bauschinger effect in atomic glasses in physical experiments on these materials at the macroscopic level.

¹⁹ Indeed, if the material is further idealized as plastically pressure-insensitive and one drops the internal variable η , then one recovers an isotropic elastic-viscoplastic constitutive model similar in form to models which are widely used for isotropic polycrystalline metallic materials (e.g. Weber and Anand, 1990).

²⁰ Which we expect our strain-softening model to capture.

²¹ Here one should bear in mind that the initial-value of the state variable s would, in general, no longer be s_0 .

$\mathbf{H} = \mathbf{H}(\mathbf{X})$ an arbitrary time-independent invertible tensor field, we may assume, without loss in generality, that

$$\mathbf{F}^p(\mathbf{X}, 0) = \mathbf{F}^{p^T}(\mathbf{X}, 0) = \mathbf{V}^p(\mathbf{X}, 0).$$

Appendix B. The constraint $\mathbf{W}^p \equiv \mathbf{0}$

We now give a formal argument demonstrating that, granted certain assumptions, a fairly general theory that allows for $\mathbf{W}^p \neq \mathbf{0}$ would result in \mathbf{W}^p small compared to \mathbf{D}^p . A theory that accounts for \mathbf{W}^p would have (3.2) replaced by

$$\text{grad} \tilde{\mathbf{v}} = \tilde{\mathbf{L}}^e + \mathbf{F}^e(\tilde{\mathbf{D}}^p + \tilde{\mathbf{W}}^p)\mathbf{F}^{e^{-1}}$$

and a term of the form $J^{-1}\mathbf{M}^p \cdot \tilde{\mathbf{W}}^p$ would be needed in (3.5). Then

$$\mathbf{T}^p \cdot \tilde{\mathbf{D}}^p + \mathbf{M}^p \cdot \tilde{\mathbf{W}}^p = J(\mathbf{F}^{e^T} \mathbf{T} \mathbf{F}^{e^{-T}}) \cdot (\tilde{\mathbf{D}}^p + \tilde{\mathbf{W}}^p)$$

would replace (3.13) and the local dissipation inequality (4.2) would have an additional term $-\mathbf{M}^p \cdot \mathbf{W}^p$ on the left side. Further, a constitutive relation for \mathbf{M}^p would be needed in (5.1), and \mathbf{T}^p , \mathbf{M}^p , and ξ^i would depend also on \mathbf{W}^p . Then (5.9) would have an additional term

$$2\text{skw}\left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p\right) \cdot \mathbf{W}^p$$

on the right side, and this leads to (5.11) augmented by the relation

$$\mathbf{M}^p = 2\text{skw}\left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p\right) + \mathbf{Y}^M(\boldsymbol{\Theta}),$$

where $\boldsymbol{\Theta}$ depends also on \mathbf{W}^p . The flow rule (6.2) would be supplemented by

$$\mathbf{S}^M - \mathbf{S}_{\text{back}}^M = \mathbf{Y}^M(\boldsymbol{\Theta}),$$

with

$$\mathbf{S}^M = \text{skw}(J\mathbf{F}^{e^T} \mathbf{T} \mathbf{F}^{e^{-T}}) = \text{skw}(\mathbf{C}^e \mathbf{T}^e), \quad \mathbf{S}_{\text{back}}^M = 2\text{skw}\left(\frac{\partial \bar{\psi}}{\partial \mathbf{B}^p} \mathbf{B}^p\right), \quad (\text{B.1})$$

and the dissipation inequality (5.12) would have the form

$$\mathbf{Y}_0(\boldsymbol{\Theta}) \cdot \mathbf{D}^p + \mathbf{Y}^M(\boldsymbol{\Theta}) \cdot \mathbf{W}^p \geq 0.$$

For special constitutive equations of the form discussed in Section 7, the relations (7.6) and (B.1)₂ yield

$$\mathbf{S}_{\text{back}}^M \equiv \mathbf{0},$$

and this leads to a pair of relations

$$\mathbf{D}^p = k_1(\Lambda) |\mathbf{S}_0 - \mu \mathbf{B}_0^p|^{(1-m)/m} (\mathbf{S}_0 - \mu \mathbf{B}_0^p),$$

$$\mathbf{W}^p = k_2(\Lambda) |\mathbf{S}^M|^{(1-m)/m} \mathbf{S}^M.$$

Thus

$$\frac{|\mathbf{W}^p|}{|\mathbf{D}^p|} = \frac{k_2(A)}{k_1(A)} \left(\frac{|\mathbf{S}^M|}{|\mathbf{S}_0 - \mu \mathbf{B}_0^p|} \right)^{1/m}. \quad (\text{B.2})$$

If we restrict attention to small elastic stretches as discussed in Section 8, then (8.3) and (8.4)₂ yield $\mathbf{S}_0 = \mathbf{O}(|\mathbf{E}^e|)$. On the other hand, since $\mathbf{C}^e \approx \mathbf{1} + 2\mathbf{E}^e$, (6.5) and (B.1)₁ imply that

$$\mathbf{S}^M \approx (\mathbf{1} + 2\mathbf{E}^e) \mathbf{T}^e (\mathbf{1} - 2\mathbf{E}^e) = \mathbf{O}(|\mathbf{E}^e|^2).$$

If we assume that $\mathbf{S}_0 - \mu \mathbf{B}_0^p$ is of the same order as \mathbf{S}_0 , which would seem reasonable, at least under monotone loading, then

$$\mathbf{S}_0 - \mu \mathbf{B}_0^p = \mathbf{O}(|\mathbf{E}^e|), \quad (\text{B.3})$$

and, by (B.2),

$$\frac{|\mathbf{W}^p|}{|\mathbf{D}^p|} = \mathbf{O}(|\mathbf{E}^e|^{1/m}).$$

Thus, granted the foregoing assumptions, for m small and k_1 and k_2 of $\mathbf{O}(1)$, we would expect \mathbf{W}^p to be small compared to \mathbf{D}^p .

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