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Computational modeling of amorphous polymers: A Lagrangian logarithmic strain space formulation of a glass-rubber constitutive model

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Abstract

We present a reformulation of the finite strain, rate dependent inelastic glass-rubber material model suggested by Buckley and Jones [1] and extended by Adams et al. [2] for modeling the deformation of amorphous polymers in the Lagrangian logarithmic strain space. This not only warrants a hyperelastic characterization in the bonding part which remedies problems associated with hypoelastic approaches devising objective stress rates selected on ad hoc basis, see, e.g., [3, 4], but also allows a transparent and naturally objective implementation analogous to the geometrically linear theory. A numerical implementation into Abaqus is pursued where algorithms for stress update and tangent moduli computations are reported. It is shown that significant reduction in nonlinear equation system size is possible in the computation of both bonding and conformational part. The characterization tests include constant-width tension, equi-biaxial tension, and simple shear. To demonstrate the robustness of the developed framework, two hypothetical problems of extreme deformation under tensile and combined tensile and torsion loading are considered. Finally, simulation of an injection stretch-blow molding process is presented as an application problem.

Keywords: glass-rubber constitutive model, viscoplasticity, amorphous glassy polymers, return mapping, Lagrangian logarithmic strains, analytical tangent, numerical tangent.

1. Introduction

Amorphous polymers hold a significant industrial importance, having applications in fibers, films, bottles [5] and medical technology [6, 7]. Amorphous polymers can undergo a reversible transition from “glass-like” to “rubber-like” mechanical behavior, the so called glass transition. This transition is typically induced by heating and cooling, where the behavior is “glass-like” below the glass transition temperature and “rubber-like” above, but can also be influenced and triggered by pressure [8], sorption [9, 10] or irradiation [11]. In processes like hot-drawing, which is commonly used to enhance the polymer’s mechanical properties such as thermomechanical stability [2, 5], glass transition may occur.

The behavior of amorphous polymers has been well documented in the literature [12–15]. Buckley and Jones [1] summarizes various physical attributes related to the deformation of uncrosslinked, amorphous polymers near the glass transition temperature. At small strains (< 0.5%), the theory of linear viscoelasticity can describe the behavior of these polymers very well. However, at larger strains, the behavior becomes non-linear viscoelastic. Furthermore, polymers also exhibit rate-dependent finite elastic-plastic behavior [16]. The temperature dependence and strain-rate sensitivity are due to the microstructure which these amorphous polymers possess in the form of an uncrosslinked network structure known as “entanglements”, posing a challenge in terms of constitutive modeling. As generally accepted, in order to induce yielding in a polymer and deform it up to large plastic strains, there are two physical resistances governing the

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energy barrier - associated with intermolecular, and intramolecular mechanisms, respectively - that need to be overcome. To induce macroscopic yielding, the stress state should be brought to a level required to overcome the intermolecular resistance. After yielding, the material starts to flow and the molecules orient themselves in the flow direction thereby decreasing the conformational entropy. Similarly to induce finite plastic deformation followed by strain hardening, the stress state should be brought to a level required to overcome the intramolecular (entropic) resistance [17]. This complexity of the behavior gives rise to the importance of having a robust three-dimensional constitutive model along with an efficient numerical implementation scheme, to be used for computational tools such as finite element modeling.

As Buckley and Jones [1] mentioned, earlier research on modeling the behavior of such polymers focused on specific mechanisms independently such as linear viscoelasticity, non-linear viscoelasticity, yield and flow, or rubber elasticity. However, those models were using viscoelastic theories - based on Eyring-type rate equations [18] - to model plastic deformation, which is restricted to a limited range of temperature and deformation rates [17]. One of the early contributions for physical based models was made by Haward et al. [19] dealing with polymers below the glass transition temperature. This was a 1D model combining yield/flow behavior based on Eyring’s [18] theory and rubber elasticity behavior based on the theory by James et al. [20], represented by a Hookean spring in series with an Eyring dashpot and rubber elasticity spring in parallel. Boyce et al. [21] extended this to a 3D constitutive model that accounts for finite viscoplastic behavior by switching from Eyring to the “double-kink model” provided by Argon [22] where a good agreement with experiments was obtained. Buckley et al. [1, 5] extended the 1D model of Haward et al. [19] to a 3D constitutive model by varying the form of flow and the rubber stress-strain relationship. A constitutive model was formulated, capable of accommodating a wide range of behaviors of polymers naturally without the need for empirical modifications on either side of the glass transition temperature. The model showed a good description of amorphous polyethylene terephthalate (PET) for strain rates around 1 s$^{-1}$ and temperatures close to glass transition. However, at large strains, there appeared to be an anomaly in comparison to experiments with regard to strain-stiffening. This was due to the assumption that the entropic “rubber-like” contribution to stress was attributed to the total stretch. Thus, an excess of drawing stress obtained from the model compared to the experiments was observed and it became more apparent at higher temperatures [2]. Buckley et al. [5] indicated this anomaly occurring due to “entanglement slippage”, and in Adams et al. [2] the glass-rubber constitutive model was extended to incorporate this feature, which is the reference point for the present work.

There exist various implementations of the glass-rubber constitutive model of Buckley and Jones [1] and its variants: Dooling et al. [23] considers infinitesimal strains whereas or Adams et al. [2] considers finite strains with irrotational deformation which allows a stretch-based multiplicative decomposition possible. Finally, [3] and and more recently [4], remedies the limitation to irrotational deformations with additive decomposition of the rate of deformation tensor and a hypoelastic characterization of the bonding part creating a requirement to devise an appropriate objective time derivative selected on an ad hoc basis. The hypoelastic characterization of the elastic response can be debated as fundamentally objectionable [24]. Such an approach keeps the spatial elasticity tensor constant and isotropic, which is not compatible with hyperelasticity [25, 26]. Moreover, hypoelasticity results in energy dissipation in closed elastic cycles [25, 26]. Finally, the objective time derivatives used in such formulations are non-unique and are not naturally motivated [27]. From the computational standpoint, the numerical integration algorithms in these formulations require careful handling of objectivity making the implementation a non-trivial task [24].

In the current framework, we remedy this shortcoming by reformulating the glass-rubber constitutive model of Buckley and Jones [1] which is later extended by Adams et al. [2] in the Lagrangian logarithmic strain space. For the bonding part, we use a hyperelastic formulation characterized by a Hencky-type isochoric strain energy function which describes elastic energy storage in terms of Lagrangian logarithmic strain deviator from which the bonding stress deviator can be computed. Thus, a selected objective spatial stress rate is not treated as an independent physical entity [26]. As a consequence, with the property that in the material configuration the material time derivative of any tensor is naturally objective, and the property where the deviatoric part of the logarithmic strain is purely isochoric, and by allowing additive decomposition of the bonding and the conformational strains into their respective parts, the use of Lagrangian logarithmic strains provides an implementation analogous to the corresponding geometrical linear theory. Our scheme
is motivated by Miehe et al. [17] where the focus was on modeling amorphous glassy polymers at a specific temperature range of interest. The strength of our reformulation lies in its simplicity and transparency. This reformulated framework (see Miehe et al. [17] for more details) consists of three major parts:

1. Geometric pre-processing, computation of the Lagrangian logarithmic strains in the material configuration, see also [28].

2. Stress- and tangent moduli-updates work-conjugate to the Lagrangian logarithmic strains in the material configuration.

3. Geometric post-processing, mapping the updated stress and tangent moduli to the current configuration, see also [28].

The structure of this contribution is as follows: In Section 2, a theoretical background and the differences between the frameworks in terms of the glass-rubber constitutive model are highlighted with remarks. In Section 3, the algorithms for the numerical implementation of the proposed reformulation are presented. In Section 4, the capability of this model to be used in an actual engineering problem (based on large strain) is carried out by using a three-dimensional finite element model. Finally, Section 5 concludes the approach and findings of this contribution.

2. Theory

2.1. Fundamental kinematics

Let\(^1\) \(\varphi(X, t)\) denote the invertible non-linear deformation map which maps points \(X \in \mathcal{B}_0\) of the reference configuration \(\mathcal{B}_0\) onto points \(x \in \mathcal{B}\) of the current configuration \(\mathcal{B}\) at time \(t \in \mathbb{R}_+\) via \(x = \varphi(X, t)\) with \(X = \varphi^{-1}(x, t)\). Then, \(F\) defines the deformation gradient and \(J\) its Jacobian determinant with

\[
F := \nabla_0 \varphi(X, t) \quad \text{and} \quad J := \det F > 0 ,
\]

where the latter is due to local impenetrability condition. The volume-preserving part of the deformation gradient is denoted by \(\tilde{F}\) where

\[
\tilde{F} := J^{-1/3}F \quad \text{and} \quad \det \tilde{F} = 1 .
\]

The right Cauchy-Green deformation tensor \(C\) and its respective volume-preserving counterpart \(\tilde{C}\) read

\[
C := F^\top \cdot F , \quad \tilde{C} := \tilde{F}^\top \cdot \tilde{F} = J^{-2/3}C \quad \text{with} \quad \det C = J^2 \quad \text{and} \quad \det \tilde{C} = 1 .
\]

Within the undeformed configuration, the deformation gradient \(F\) has the following unique polar decomposition

\[
F = R \cdot U ,
\]

\(^1\)The following notation is used: Definitions are denoted by :=. Assuming \(a, b,\) and \(c\) as three second-order tensors, together with the Einstein’s summation convention on repeated indices, \(c = a \cdot b\) represents the product with \(c_{ik} = a_{ij}b_{jk}\), \(d = a : b = a_{ij}b_{ij}\) represents the inner product where \(d\) is a scalar. \(E = a \otimes b\) represents the tensor product with \(E_{ijkl} = a_{ij}b_{kl}\) where \(E\) is a fourth-order tensor. \(I\) is the fourth-order symmetric identity tensor where \(I := 1/2[\delta_{ik}\delta_{lj} + \delta_{lj}\delta_{ik}]\) and \(\mathcal{I}\) is the fourth-order projection tensor where \(\mathcal{I} := [-1/3\delta_{ij}\delta_{kl} + 1/2\delta_{ik}\delta_{lj} + 1/2\delta_{il}\delta_{jk}]\). \(\mathfrak{e}_i \otimes \mathfrak{e}_j \otimes \mathfrak{e}_k \otimes \mathfrak{e}_l\) and \(|\cdot| := \text{dev}\; (\cdot) := |\cdot| - 1/3 \text{tr}(\cdot) I\) and \(\text{tr}\; (\cdot)\) stand for the deviatoric part of and trace of a second-order tensor \(|\cdot|\), respectively, with \(I\) denoting the second-order identity tensor, \(\text{sym}\; (\cdot)\) and \(\text{skw}\; (\cdot)\) respectively denote symmetric and skew-symmetric parts of a second-order tensor \(|\cdot|\) with \(\text{sym}\; (\cdot) := 1/2[|\cdot| + |\cdot|^\top]\) and \(\text{skw}\; (\cdot) := 1/2[|\cdot| - |\cdot|^\top]\). \(|\cdot|\) gives the material time derivative of \(|\cdot|\). \(|\cdot|^\top\) and \(|\cdot|^{-1}\) denote the transpose and the inverse of \(|\cdot|\), respectively. \(\text{Div}\; (\cdot)\) designates the divergence operator with respect to the coordinates in the reference configuration. Analogously, \(\nabla_0\; (\cdot)\) designates the gradient operator with respect to the coordinates in the reference configuration. \(\ln\; (\cdot)\) represents natural logarithm. Square brackets \([\ldots]\) are used to collect mathematical expressions and components in explicit vector and matrix representations whereas round brackets \((\ldots)\) represent function arguments.
where $\mathbf{U}$ represents the unique positive definite, symmetric right stretch tensor such that $\mathbf{U}^2 = \mathbf{C}$ and $\mathbf{R}$ is a proper orthogonal rotation tensor with $\det \mathbf{R} = 1$. The Lagrangian logarithmic strain tensor $\epsilon$ is given by

$$\epsilon = \sum_{A=1}^{3} \epsilon_A \mathbf{P}_A \quad \text{with} \quad \mathbf{P}_A = \mathbf{N}_A \otimes \mathbf{N}_A, \quad A = 1, 2, 3,$$

(5)

where $\mathbf{N}_A$ are the referential principal directions and $\epsilon_A$ are the corresponding eigenvalues associated with $\epsilon$. Let $\mathbf{C}_A$ denote the eigenvalues of $\mathbf{C}$, then the following relations apply

$$\epsilon := \frac{1}{2} \ln \mathbf{C} \quad \text{and} \quad \epsilon_A := \ln \lambda_A \quad \text{with} \quad \lambda_A := \sqrt{\mathbf{C}_A} \quad \text{and} \quad \lambda_1 \lambda_2 \lambda_3 = J,$$

(6)

$$\tilde{\epsilon} := \frac{1}{2} \ln \tilde{\mathbf{C}} \quad \text{and} \quad \tilde{\epsilon}_A := \ln \tilde{\lambda}_A \quad \text{with} \quad \tilde{\lambda}_A := \sqrt{\tilde{\mathbf{C}}_A} \quad \text{and} \quad \tilde{\lambda}_1 \tilde{\lambda}_2 \tilde{\lambda}_3 = 1.$$

(7)

Here, $\tilde{\epsilon}$ denotes the volume-preserving part of the Lagrangian logarithmic strains with corresponding eigenvalues $\tilde{\epsilon}_A$. Similarly, $\mathbf{C}_A$ denote the eigenvalues of $\mathbf{C}$. $\lambda_A$ are referred to as principal stretches, whereas $\tilde{\lambda}_A$ refers to their isochoric counterparts. Since

$$\text{tr} \, \epsilon = \ln \lambda_1 + \ln \lambda_2 + \ln \lambda_3 = \ln(\lambda_1 \lambda_2 \lambda_3) = \ln J,$$

(8)

$$\text{tr} \, \epsilon$$

and $\ln J$ can be used interchangeably. Finally, the following identity applies

$$\tilde{\epsilon} = \epsilon \equiv \text{dev} \, \epsilon = \epsilon - \frac{1}{3} \ln J \mathbf{1}.$$

(9)

Thus, as in the case for infinitesimal strain tensor, the deviatoric part of the logarithmic strain is purely isochoric. Considering the formulation presented in [3], we also introduce the following rate-type kinematic measures. Let $\mathbf{L} = \mathbf{L}(\mathbf{x}, t)$ denote the spatial velocity gradient where $\mathbf{L} := \nabla, \mathbf{v}(\mathbf{x}, t)$ and with $\mathbf{v}(\mathbf{x}, t) = \dot{\mathbf{x}}(\mathbf{v}^{-1}(\mathbf{x}, t), t)$ representing the spatial description of the velocity vector. The rate of deformation tensor $\mathbf{D}$ and the spin tensor $\mathbf{W}$ are, then, defined by splitting $\mathbf{L}$ into its symmetric and skew-symmetric parts with $\mathbf{D} := \text{sym}(\mathbf{L})$ and $\mathbf{W} := \text{skw}(\mathbf{L})$.

2.2. Glass-rubber constitutive model

The model initially proposed by Buckley and Jones [1] (and modified by Adams et al. [2]) is based on the key assumption that the total stress can be additively decomposed into two parts: a bonding and a conformational part. The interaction of these two parts can be understood by considering a parallel coupling between them where each arm of the coupling consists of an elastic spring (linear for bonding and non-linear for conformational) and a viscous damper, as shown in Figure 1. On the bonding arm, the linear elastic spring and the viscous dashpot represent the bond stretching, and the bond deformation and breakage, respectively. On the conformational arm, the non-linear elastic spring and the viscous dashpot denote the stretching of the entanglement and the flow of the entanglement network, respectively. The bonding and conformational parts act independent of each other but are subjected to the same deformation [3] expressed by the deformation gradient tensor $\mathbf{F}$. Thus, we write:

$$\mathbf{F} = \mathbf{F}^b = \mathbf{F}^c,$$

(10)

where the superscripts $b$ and $c$ represent bonding and conformational parts, respectively. Associated Lagrangian logarithmic strains are given by:

$$\epsilon = \epsilon^b = \epsilon^c.$$

(11)

The response at the glassy state (where bonding stress is dominant) is not perfectly elastic. A viscoelastic contribution is essential along with elastic distortion to account for the complete deformation [3]. Hence, the bonding strain tensor $\epsilon^b$ is additively decomposed into elastic $\epsilon^e$ and viscoplastic $\epsilon^p$ parts [3, 29]. Similarly, to account for the flow of the network because of entanglement slippage, the conformational strain tensor $\epsilon^c$ is additively decomposed into network stretch $\epsilon^s$ and slippage of entanglement parts $\epsilon^d$ [3]:

$$\epsilon^b = \epsilon^e + \epsilon^p \quad \text{and} \quad \epsilon^c = \epsilon^n + \epsilon^d.$$

(12)
In the above expression, the entanglement and modulus, \( \Theta \) is the absolute temperature, and network stretch dependent variables with the constants \( \tau \) additively split into bonding stress temperature \( \Theta \) respectively, of each component. The part of the constitutive model that is dominant, depends strongly on the glass transition spring (linear for bonding and non-linear for conformational) and viscous dashpot on each arm depict the stretching and flow, and Jones [1] and Adams et al. [2]. The parallel arms represent the bonding and conformational part, whereas the elastic Figure 1: A rheological model representing the behavior of a class of amorphous glassy polymers as suggested by Buckley and Jones [1] and Adams et al. [2]. The parallel arms represent the bonding and conformational part, whereas the elastic springs (linear for bonding and non-linear for conformational) and viscous dashpot on each arm depict the stretching and flow, and the work conjugate stress to Lagrangian logarithmic strains is denoted by \( \lambda \).

Remark: In their original formulation, Adams et al. [2] consider irrotational displacements of the PET film which is described by a stretch tensor \( \Lambda \) whose eigenvalues are the principal stretches \( \lambda_A \) for \( A = 1, 2, 3 \). They, then, postulate a multiplicative decomposition for the bonding part in terms of elastic and viscous stretches with \( \lambda_A^b = \lambda_A^s \lambda_A^b \), and for the conformational part in terms of network and slippage stretches with \( \lambda_A^c = \lambda_A^s \lambda_A^c \) for \( A = 1, 2, 3 \). The additive decomposition in Lagrangian logarithmic strains naturally satisfies this multiplicative decomposition under identical conditions. Considering rotational displacements, Dooling et al. [3] extended this framework by postulating rate additivity in bonding rate of deformation tensor via \( \dot{D}^b = \dot{D}^c + \dot{D}^v \) as well as rate additivity in conformational rate of deformation tensor via \( \dot{D}^e = \dot{D}^u + \dot{D}^z \). Taking the material time derivatives of the strain partitions given in Eq. (12), one reaches a rate additive form in Lagrangian logarithmic strains with \( \dot{\epsilon}^b = \dot{\epsilon}^c + \dot{\epsilon}^v \) and \( \dot{\epsilon}^e = \dot{\epsilon}^u + \dot{\epsilon}^z \).

The work conjugate stress to Lagrangian logarithmic strains is denoted by \( \tau \) and is assumed to be additively split into bonding stress \( \tau^b \) and conformational stress \( \tau^c \).

\[
\tau = \tau^b + \tau^c.
\]  

Buckley and Jones [1] discussed the problem of having no physical model available for the development of conformational entropy as a function of molecular mobility through glass transition temperatures. It was assumed that this molecular mobility is fully developed and thus a physical theory, presented by Edward et al. [30, 31] which justifies this assumption, was used. The free energy function \( \Psi^c \) in the Lagrangian configuration for cross-linked, entangled polymers reads

\[
\Psi^c (\lambda_1^n, \lambda_2^n, \lambda_3^n) := D \left[ E \frac{\xi (\lambda_1^n, \lambda_2^n, \lambda_3^n)}{\zeta (\lambda_1^n, \lambda_2^n, \lambda_3^n)} + \phi (\lambda_1^n, \lambda_2^n, \lambda_3^n) + \ln \zeta (\lambda_1^n, \lambda_2^n, \lambda_3^n) \right],
\]

with the constants

\[
D := \frac{N_v k_b \Theta}{2} \quad \text{and} \quad E := [1 + \eta] \left[ 1 - \alpha^2 \right],
\]

and network stretch dependent variables

\[
\zeta (\lambda_1^n, \lambda_2^n, \lambda_3^n) := 1 - \alpha^2 \left[ [\lambda_1^n]^2 + [\lambda_2^n]^2 + [\lambda_3^n]^2 \right],
\]

\[
\xi (\lambda_1^n, \lambda_2^n, \lambda_3^n) := \frac{[\lambda_1^n]^2}{1 + \eta [\lambda_1^n]^2} + \frac{[\lambda_2^n]^2}{1 + \eta [\lambda_2^n]^2} + \frac{[\lambda_3^n]^2}{1 + \eta [\lambda_3^n]^2},
\]

\[
\phi (\lambda_1^n, \lambda_2^n, \lambda_3^n) := \ln \left( 1 + \eta [\lambda_1^n]^2 \right) + \ln \left( 1 + \eta [\lambda_2^n]^2 \right) + \ln \left( 1 + \eta [\lambda_3^n]^2 \right).
\]

In the above expression, \( N_v \) denotes the density of the slip links representing entanglements, \( k_b \) is the bulk modulus, \( \Theta \) is the absolute temperature, \( \eta \) is a parameter specifying the looseness or the axial mobility of the entanglement and \( \alpha \) presents a measure of inextensibility of the entanglement network.
Remark: The response of this model at the rubbery state (where conformational stress is dominant) was initially assumed perfectly elastic [1]. However, the elastic stretch can not account for the temperature dependence observed during experiments at elevated temperatures [1, 2]. At these temperatures, a stress deficit was observed since the strain resulting from entanglement slippage reduces the network strain for a given total strain and thus reduces the conformational stress. Hence, Adams et al. [2] proposed that the total stretch can be expressed in terms of elastic network stretch and flow because of slippage of the entanglements. It was further observed that there seemed to be an arrest of the slippage stretch at a certain value of stress for each temperature. Adams et al. [2] computed the network stretches corresponding to the stress values given total strain and thus reduces the conformational stress. Hence, Adams et al. [2] proposed that the total stretch can be expressed in terms of elastic network stretch and flow because of slippage of the entanglements.

The viscosity, \( \gamma \), in Eq. (21) tends to increase asymptotically (demonstrating the arrest of the slippage strain) with the development of molecular orientation [2]. The viscosity \( \gamma \) is related to critical stretch \( \lambda^{\text{crit}} \) via a two-parameter expression in order to be consistent with the experimental results:

\[
\gamma := \gamma_0 \frac{\lambda^{\text{crit}} - 1}{\lambda^{\text{crit}} / \lambda^{n,\text{max}} - 1},
\]

(22)

Note that \( \gamma \to \infty \) as \( \lambda^{n,\text{max}} \to \lambda^{\text{crit}} \). The temperature-dependent slippage viscosity \( \gamma_0 \) is calculated by the Fulcher equation [3, 12] as

\[
\gamma_0 := \gamma^* \exp \left( \frac{C^s}{\Theta - \Theta^\infty} - \frac{C^s}{\Theta^* - \Theta^\infty} \right).
\]

(23)

Here, \( \gamma^* \) is the slippage viscosity at a reference temperature \( \Theta^* \), and \( C^s \), the slippage viscosity constant, and \( \Theta^\infty \), the limiting temperature, are material constants used to obtain best-fit curves for the slippage viscosity in the conformational part at various temperatures [2]. Note that in Eq. (23), \( C^s \sim \gamma_0 \), therefore the slippage viscosity constant directly makes the response of the material stiff, while as \( \Theta^\infty \to \Theta^* \), \( \gamma_0 \to 0 \).

The bonding stress is expressed in terms of the strain-induced hydrostatic and the deviatoric parts

\[
\tau^b = \frac{1}{3} \text{tr}(\tau^b) + \overline{\tau^b} \mathbf{1} = [\kappa \ln J + \tau^{b,\text{m0}}] \mathbf{1} + \overline{\tau^b},
\]

(24)
where $\kappa$ is the bulk modulus and $\tau^{b,m0}$ the initial, built-in bond stretching stress, resisting the collapse of the entropic network [2] which is determined via [1]:

$$\tau^{b,m0} = -N^s k^b \Theta \left[ \frac{1 + \alpha^2}{1 - 3\alpha^2} + \frac{\eta}{1 + \eta} \right].$$

The stress deviator in Eq. (24) is computed using total elastic strain tensor with $\overline{\tau}^b = 2 G^b \overline{e}$ where $G^b$ denotes the shear modulus. The rate of the Lagrangian logarithmic strains associated with viscous part is computed through a non-Newtonian flow

$$\dot{\overline{e}}^\eta = \frac{\overline{\tau}^b}{2 G^b \tau^\eta}.$$  

Considering that $\overline{\tau} = \overline{\tau}^b = \overline{e}^\eta + \overline{e}^\tau$, the following relation applies

$$\overline{\tau}^b + \frac{\overline{\tau}^b}{\tau^\eta} = 2 G^b \dot{\overline{e}}.$$  

Remark: Dooling et al. [3] express the viscous part in the bonding rate of strain tensor deviator in $\overline{D}^\eta = \overline{D}^\eta + \overline{D}^\tau$ with $\overline{D}^\eta = \overline{\sigma}^\eta / 2 G^b \tau^\eta$. Coming to the elastic part, a hypoelastic description is pursued with $\overline{\nabla} \overline{\sigma}^\eta = 2 G^b \overline{D}^\tau$ where $\overline{\sigma}^\eta = \overline{\sigma}^\eta - \mathbf{W} \cdot \overline{\sigma}^\eta + \overline{\sigma}^\eta \cdot \mathbf{W}$ denotes the objective Jaumann rate of the (spatial) Cauchy-type bonding stress, selected among other objective stress rates on an ad hoc basis. Hypoelastic frameworks are known to keep the spatial elasticity tensor constant and isotropic, which does not allow a stored energy function to exist and hence is not compatible with hyperelasticity [25, 26]. Hypoelasticity also precludes modeling elasticity in the nonlinear range, e.g., closed elastic cycles results in energy dissipation [25, 26]. Our treatment, on the other hand, corresponds to a hyperelastic formulation characterized by a Hencky-type isochoric strain energy function which describes elastic energy storage in terms of Lagrangian logarithmic strain deviator, so that the stored energy function $\Psi^{iso}(\overline{e}^\tau)$ exists with: $\Psi^{iso}(\overline{e}^\tau) = G^b \overline{e} : \overline{e}^\tau$. Thus, one computes the corresponding stress with $\overline{\tau}^\tau = \partial \Psi^{iso}(\overline{e}^\tau) / \partial \overline{e}^\tau = 2 G^b \overline{e}^\tau$. As a consequence, material or spatial stress rates appear as a natural consequence of the consistent linearization and not treated as an independent physical entity [26]. Although, the glass-rubber model is not derived based on the thermodynamics of irreversible processes like in the works of, e.g., Maurel-Pantel [32] and Gudimetla et al. [33], with a hyperelasticity-based bonding stress definition, it does not violate the second principle of thermodynamics, that is, it satisfies the Clausius-Duhem inequality by providing a positive inelastic dissipation.

In Eqs. (26) and (27), $\tau^\eta = \frac{\mu}{2 G^b}$ is the relaxation time and $\mu$ the viscosity given by

$$\mu := \mu_0 \Omega \frac{\Xi}{\sinh(\Xi)} \quad \text{with} \quad \Xi := \frac{V^s \tau^{b,oct}}{2 R \Theta} \quad \text{and} \quad \Omega := \exp\left( -\frac{V^p \tau^{b,mean}}{R \Theta} \right).$$

The limiting cases for the above equation are then

$$\frac{\Xi}{\sinh(\Xi)} \to 1 \quad \text{one has} \quad \mu \to \mu_0 \Omega \quad \text{as} \quad \Xi \to 0 \quad \text{and} \quad \frac{\Xi}{\sinh(\Xi)} \to 0 \quad \text{one has} \quad \mu \to 0 \quad \text{as} \quad \Xi \to \infty,$$

which are critical with respect to the numerical implementation. Here, $V^s$ and $V^p$ are the shear and pressure activation volumes, respectively, $R$ the gas constant, $\tau^{b,mean} := k^b \ln J$ the mean bonding stress increment and $\tau^{b,oct} := 1 / \sqrt[3]{\left[ \overline{\tau}^b : \overline{\tau}^b \right]^{1/2}}$ the octahedral shear stress. In Eq. (28), $\mu_0$ is the viscosity in the low stress (Newtonian) limit

$$\mu_0 := \mu^* \exp\left( \frac{C}{\Theta - \Theta^*} - \frac{C}{\Theta^* - \Theta^*} + \frac{\Delta H_0}{R \Theta} \frac{\Delta H_0}{R \Theta^*} \right),$$

where $\mu^*$ is the viscosity at a reference temperature $\Theta^*$. 

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The constitutive model by Buckley et al. [1, 5] exhibits various features of amorphous polymers near glass transition temperature such as yield region followed by flow and strain stiffening. However, there were two major differences between experiments and simulations: the region of the simulated yield being narrow, and the convergence of stress-strain curves at large strains at various temperatures. The narrow simulated yield region is, firstly, a well-known aspect of Eyring type constitutive models and, secondly, instead of existence of a wide range of activation energies in the linear viscoelastic range (and hence a spectrum of relaxation times), this model assumes only one activation energy (and, hence, a single relaxation time) [5]. Hasan et al. [34] incorporated a wide range of activation energies which lead to the broadening of the yield region. The convergence of the stress-strain curves at large strain is because of the omission of the contribution of slippage strains to conformational stress, which was taken care by Adams et al. [2].

3. Finite element implementation

In view of quasi-static conditions, the local material form of the balance of linear momentum

$$\text{Div} (\mathbf{F} \cdot \mathbf{S}) + \rho_0 \mathbf{b} = \mathbf{0},$$

yields the following material principle of virtual work in terms of the second Piola-Kirchhoff tensor $\mathbf{S}$

$$G(\varphi, \delta \varphi) := \int_{B_0} \mathbf{S} : \delta \mathbf{E} \, dV_0 - \left[ \int_{\partial B_0} \rho_0 \mathbf{b} \cdot \delta \varphi \, dV_0 + \int_{\partial B_0} \mathbf{t} \cdot \delta \varphi \, dA_0 \right] = 0.$$  \hspace{1cm} (32)

Considering a trial solution $\varphi_h$, the above equation can be linearized in the direction of an increment $\mathbf{u}$ in $\varphi_h$ as $G(\varphi_h, \delta \varphi) + \langle D_\varphi G(\varphi_h, \delta \varphi); \mathbf{u} \rangle = 0$ with $\langle D_\varphi G(\varphi_h, \delta \varphi); \mathbf{u} \rangle$ denoting the Gâteaux derivative with respect to $\varphi$ at $\varphi = \varphi_h$ in the direction of $\mathbf{u}$. The linearization of the equilibrium equation is considered in terms of the internal and external virtual work components as

$$\langle D_\varphi G(\varphi_h, \delta \varphi); \mathbf{u} \rangle = \langle D_\varphi W_{\text{int}}(\varphi_h, \delta \varphi); \mathbf{u} \rangle + \langle D_\varphi W_{\text{ext}}(\varphi_h, \delta \varphi); \mathbf{u} \rangle.$$  \hspace{1cm} (33)

Leaving the linearization of the external virtual work out, noting that a virtual velocity $\delta \varphi$ is associated with every particle $\mathbf{X}$ in the body, and it is not allowed to alter during the incremental change $\mathbf{u}$ and using the product rule for directional derivatives and the definition of the material elasticity tensor, the Gâteaux derivative is obtained as

$$\langle D_\varphi W_{\text{int}}(\varphi_h, \delta \varphi); \mathbf{u} \rangle = \int_{B_0} \delta \mathbf{E} : \langle D_\varphi (\mathbf{S}); \mathbf{u} \rangle \, dV_0 + \int_{\partial B_0} \langle D_\varphi (\delta \mathbf{E}); \mathbf{u} \rangle : \mathbf{S} \, dA_0.$$  \hspace{1cm} (34)

The first part on the right-hand side is due to material stiffness and the second part due to initial stress. Using the chain rule, a linear relationship between the directional derivative of $\mathbf{S}$ and the linearized strain $\langle D_\varphi (\mathbf{E}); \mathbf{u} \rangle$ can be obtained as

$$\langle D_\varphi (\mathbf{S}); \mathbf{u} \rangle = \mathbf{C} : \langle D_\varphi (\mathbf{E}); \mathbf{u} \rangle \quad \text{with} \quad \mathbf{C} = \frac{\partial \mathbf{S}}{\partial \mathbf{E}},$$  \hspace{1cm} (35)

where $\mathbf{C}$ denotes the Lagrangian tangent tensor. Noting the symmetry of $\mathbf{S}$, yields the Lagrangian linearized principle of virtual work as

$$\langle D_\varphi W_{\text{int}}(\varphi_h, \delta \varphi); \mathbf{u} \rangle = \int_{B_0} \mathbf{S} : \{[\nabla_0 \mathbf{u}]^T \cdot \nabla_0 \delta \varphi \} \, dV_0 + \int_{\partial B_0} \delta \mathbf{E} : \mathbf{C} : \langle D_\varphi (\mathbf{E}); \mathbf{u} \rangle \, dA_0.$$  \hspace{1cm} (36)

The term $\nabla_0 \delta \varphi$ remains constant because the virtual velocities are not a function of the configuration. Considering

$$\delta \mathbf{E} : \mathbf{C} : \langle D_\varphi (\mathbf{E}); \mathbf{u} \rangle \, dV_0 = \delta \mathbf{d} : \mathbf{e} \, dV,$$  \hspace{1cm} (37)
with \(2\delta d = \nabla v_1 \partial v + [\nabla v_1 \delta v]^\top\) and \(2e = \nabla v + [\nabla v]^\top\), one can push forward the material constitutive tensor \(C\) to obtain the spatial one \(c\) using

\[
c_{ijkl} = \frac{1}{J} F_{ik} F_{jl} F_{kJL} C_{ijkl},
\]

(38)

which yields the Eulerian linearized internal virtual work

\[
\langle D_\varphi W_{\text{int}}(\varphi, \delta v); u \rangle = \int_B \sigma : [\nabla v]^\top \cdot \nabla \delta v] \, dV + \int_B \delta d : e \cdot e \, dV.
\]

(39)

Using indicial notation and considering that \(\partial \tau / \partial C = \partial \tau / \partial \epsilon : \partial \epsilon / \partial C\) with \(\tau = \tau(\epsilon)\) with \(\tau = JR^{-1} \cdot \sigma \cdot R\) and \(S = JF^{-1} \cdot \sigma \cdot F^{-1}\) which allows us to obtain \(S = U^{-1} \cdot \tau \cdot U^{-\top}\), we compute the components of \(C\) with

\[
C_{ijkl} = 2U_{IM}U_{JN} \frac{d \epsilon_{RS}}{d \sigma_{KL}} \frac{\partial C_{KL}}{\partial C_{RS}} + \left[ 2 \frac{\partial U_{IM}}{\partial C_{KL}} U_{JN}^{-1} + 2U_{IM} \frac{\partial U_{JN}^{-1}}{\partial C_{KL}} \right] \tau_{MN}.
\]

(40)

Hence, considering that \(U^{-1} = C^{-1/2}\) and \(\epsilon = 1/2 \ln C\), one can use the representations

\[
U^{-1} = f(C) = \sum_{A=1}^{3} \gamma_{A} \rho_{A} \quad \text{and} \quad \epsilon = h(C) = \sum_{A=1}^{3} \lambda_{A} \rho_{A}.
\]

(41)

Now, for a tensor-valued function \(g(A)\) acting over a symmetric second-order tensor \(A\) with

\[
g(A) = \sum_{A=1}^{3} \gamma_{A} \rho_{A} \quad \text{with} \quad A = \sum_{A=1}^{3} \lambda_{A} \rho_{A},
\]

(42)

considering distinct eigenvalues, one has, see, e.g., [35],

\[
\frac{\partial g(A)}{\partial A} = \sum_{A=1}^{3} \gamma_{A} \rho_{A} \otimes \rho_{A} + \sum_{A,B=1,A \neq B}^{3} \frac{\gamma_{A} - \gamma_{B}}{\lambda_{A} - \lambda_{B}} \rho_{A} \otimes \rho_{B} \, \text{P}^{\text{sym}},
\]

(43)

where \(\text{P}^{\text{sym}} = [\rho_{A} \otimes \rho_{B}]^{\text{sym}}\) represents the symmetric version of the fourth-order tensor \(\text{P}\), with components \(\text{P}_{ijkl}^{\text{sym}} = 1/2 \, [\rho_{IK} \rho_{JL} + \rho_{IL} \rho_{JK}]\). This allows the computation of \(\partial U^{-1} / \partial C = \partial \gamma(C) / \partial C\) and \(\partial \epsilon / \partial C = \partial h(C) / \partial C\) to give

\[
\frac{\partial U^{-1}}{\partial C} = \frac{\partial f(C)}{\partial C} = \sum_{A=1}^{3} \gamma_{A} \rho_{A} \otimes \rho_{A} + \sum_{A,B=1,A \neq B}^{3} \frac{\gamma_{A} - \gamma_{B}}{\lambda_{A} - \lambda_{B}} \rho_{A} \otimes \rho_{B} \, \text{P}^{\text{sym}};
\]

(44)

and

\[
\frac{\partial \epsilon}{\partial C} = \frac{\partial h(C)}{\partial C} = \sum_{A=1}^{3} \lambda_{A} \rho_{A} \otimes \rho_{A} + \sum_{A,B=1,A \neq B}^{3} \frac{\lambda_{A} - \lambda_{B}}{\lambda_{A} - \lambda_{B}} \rho_{A} \otimes \rho_{B} \, \text{P}^{\text{sym}},
\]

(45)

with

\[
f(\lambda_{A}) = \frac{1}{\lambda_{A}} \quad \text{and} \quad h(\lambda_{A}) = \frac{1}{2} \ln(\lambda_{A}^{2}) = \ln(\lambda_{A}) .
\]

(46)

\footnote{Subscript \(J\) should not be confused with \(J' := \text{det} \, F\).}

\footnote{Eqs. (44) and (45) suffer from singularity or ill-conditioning for equal or nearly equal eigenvalues, respectively, where \(\lambda_{A} - \lambda_{B} \to 0\). The analytical treatment of such cases in the context of finite elasticity materializing the Hospital rule is given in Appendix B.}
Using \( f'(\lambda_A^2) = 1/2\lambda_A \partial f(\lambda_A^2) / \partial \lambda_A \) and \( h'(\lambda_A^2) = 1/2\lambda_A \partial h(\lambda_A^2) / \partial \lambda_A \) leads to

\[
f'(\lambda_A^2) = -\frac{1}{2\lambda_A} \quad \text{and} \quad h'(\lambda_A^2) = \frac{1}{2\lambda_A^3}.
\]  

(47)

With the standard relations \( \partial e_{RS} / \partial C_{KL} \) and \( \partial U_{IM}^{-1} / \partial C_{KL} \) computed in view of Eqs. (44) and (45), what is left to compute is only the stress \( \tau \) and tangent modulus \( d\tau / d\epsilon \). Considering a standard time interval \([t_n, t_{n+1}]\), using the notation \( \Delta t = t_{n+1} - t_n \), and denoting any state variable at the beginning and the end of the interval with subscripts \( n \) and \( n+1 \), respectively, these computations are elaborated in the following.

### Algorithm 1: Stress update and tangent computation

1. **Input arguments:** \( \Delta t, F_n, F \), internal variables \( \mathcal{I}_n \).
2. **Geometric pre-processing:** Compute right Cauchy-Green deformation tensor \( C \) using Eq. (3), Lagrangian logarithmic strain \( \epsilon \) using Eq. (6) and rotation tensor \( R \) using Eq. (4) where \( U = \sqrt{C} \).
3. **Core computations:** Obtain rotated Kirchhoff-type bonding stress \( \tau^b \) and bonding tangent \( d\tau^b / d\epsilon \) from Algorithm 2 and conformational Kirchhoff stress \( \tau^c \) and conformational tangent \( d\tau^c / d\epsilon \) from Algorithm 3 to form the rotated Kirchhoff-type total stress with \( \tau = \tau^b + \tau^c \) and total tangent with \( d\tau / d\epsilon = d\tau^b / d\epsilon + d\tau^c / d\epsilon \).
4. **Geometric post-processing:** Rotate back and scale rotated Kirchhoff-type total stress to obtain total Cauchy stress with \( \sigma = 1/J R \cdot \tau \cdot R^T \) and also compute \( c \) by transforming \( d\tau / d\epsilon \) using Eqs. (38) and (40) along with Eqs. (44) and (45).

#### 3.1. Algorithmic treatment of bonding stress \( \tau^b \)

In order to obtain \( \tau^b \) in step 2 of Algorithm 1, its volumetric and deviatoric part is required. The volumetric part of \( \tau^b \) can be computed trivially using Eq. (24). However, for the deviatoric part, it is required to use an iterative scheme. In order to do so, we integrate Eq. (27) using a backward-Euler scheme and taking into consideration the dependence of \( \mu \) on \( \tau^{b, \text{oct}} \)

\[
\tau^b = \frac{\mu}{\mu + 2G^{b}\Delta t} \left[ \frac{\tau^b}{\tau^b_n} + 2G^{b}\Delta \epsilon \right].
\]

(48)

Setting \( \varsigma := \tau^b_n + 2G^{b}\Delta \epsilon \), taking the norm of both sides, multiplying both sides by 1/3 and taking their roots in Eq. (48), while using \( \varsigma := 1/\sqrt{3} [\varsigma : \varsigma]^{1/2} \), the following relation is derived

\[
\tau^{b, \text{oct}} = \frac{\mu (\tau^{b, \text{oct}})}{\mu (\tau^{b, \text{oct}}) + 2G^{b}\Delta t} \varsigma.
\]

(49)
In contrast to Eq. (48), Eq. (49) comprises only a scalar unknown requiring the following residual to be solved, which is non-linear in $\tau^{b,\text{oct}}$

$$r(\tau^{b,\text{oct}}) = \tau^{b,\text{oct}} - \frac{1}{1 + \frac{2G^b}{\mu} \Delta t} \varsigma = 0. \quad (50)$$

This kind of transformation of a tensor quantity to a scalar quantity has not been used in the available glass-rubber constitutive models such as [1, 2, 23]. This also allows non-linearities in Eq. (28) to be computed at each step unlike in the work of Dooling et al. [23] and Li et al. [4]. Eq. (50) is nonlinear in $\tau^{b,\text{oct}}$ and for its solution a Newton-Raphson scheme is devised where the details are given in Appendix D.1.

3.1.1. Derivation of the consistent inelastic moduli for the bonding stress $d\tau^b/d\epsilon$

Using the following derivations

$$\frac{\partial \mu}{\partial \tau^b} = \frac{\partial \mu}{\partial \tau^{b,\text{oct}}} \frac{\partial \tau^{b,\text{oct}}}{\partial \tau^b} = \omega \frac{\tau^b}{3\tau^{b,\text{oct}}} \quad \text{and} \quad \frac{\partial \Delta \epsilon}{\partial \epsilon} = \mathbb{I}, \quad (51)$$

where $\omega$ can be obtained through Eq. (D.5). While applying implicit differentiation to Eq. (48), we obtain

$$\frac{d\tau^b}{d\epsilon} = \frac{2G^b}{2G^b \Delta t + \mu} \left[ I - \vartheta \tau^b \otimes \tau^b \right]^{-1} : \mathbb{I}, \quad (52)$$

with

$$\vartheta = \frac{\omega G^b \Delta t}{3 \mu \tau^{b,\text{oct}} [2G^b \Delta t + \mu]}. \quad (53)$$

Applying the Sherman-Morrison-Woodbury formula [37] in computation of the inverse of the expression in the brackets in Eq. (52) we obtain $d\tau^b/d\epsilon$ which shows both minor and major symmetries. Considering the hydrostatic part as well, the total tangent due to bonding contribution reads

$$\frac{d\tau^b}{d\epsilon} = \kappa \mathbf{1} \otimes \mathbf{1} + \frac{2G^b}{2G^b \Delta t + \mu} \left[ I + \varrho \tau^b \otimes \tau^b \right], \quad (54)$$

with

$$\varrho = \frac{\vartheta}{1 - 3 \varrho [\tau^{b,\text{oct}}]^2}. \quad (55)$$

Algorithm 2 shows the procedure to obtain the bonding stress $\tau^b$ and the corresponding tangent $d\tau^b/d\epsilon$.

**Algorithm 2** Computation of bonding stress $\tau^b$ and tangent $d\tau^b/d\epsilon$

1. Input arguments: $\Delta t$, $\epsilon_0$, $\epsilon$, $\Theta$, internal variables $I_n$.
2. Given material properties: $\kappa$, $G^b$, $\mu^*$, $C$, $\Theta^\infty$, $\Theta^*$, $R$, $\Delta H_0$, $V^s$, $V^p$, $\alpha$, $\eta$, $N^s$, $k^b$.
3. Calculate initial resistance $\tau^{b,\text{m0}}$ using Eq. (25).
4. Calculate reference viscosity $\mu_0$ using Eq. (30).
5. Calculate deviatoric strain $\mathbf{\varepsilon}$ using Eq. (9).
6. Compute residuum $r$ using Eq. (50).
7. Calculate updated octahedral bonding stress: $\tau^{b,\text{oct}}_{i+1} = \tau^{b,\text{oct}}_i + \Delta \tau^{b,\text{oct}}$ using Eq. (D.2).
   \[ \text{IF } |r| < TOL \quad \text{CONTINUE} \]
   \[ \text{OTHERWISE Go To step 6} \]
8. Calculate the viscosity $\mu$ using Eq. (28).
9. Calculate bonding stress $\tau^b$ using Eqs. (24) and (48).
10. Calculate tangent $d\tau^b/d\epsilon$ using Eq. (54).
11. Return $\tau^b$ and $d\tau^b/d\epsilon$. 

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3.2. Algorithmic treatment of conformational stress $\tau^c$

Similarly, in order to obtain $\tau^c$ in step 2 of Algorithm 1, the use of an iterative scheme is required and, thus, integration of Eq. (21) is carried out using a backward-Euler scheme

$$\Delta \varepsilon^e_{A} = \Delta t \frac{\tau^c_A}{\gamma} .$$  

(56)

Adopting an elastic-predictor-plastic corrector algorithm and defining the elastic trial state as $\Delta \varepsilon \to \Delta \varepsilon^{n,tri}$, the trial network strain and the trial conformational stress $\tau^{c,tri}$ can be computed as

$$\varepsilon^{n,tri} = \varepsilon^n + \Delta \varepsilon = \sum_{A=1}^{3} \varepsilon^{n,tri}_A P^A_{n,tri}$$

and

$$\tau^{c,tri} = \sum_{A=1}^{3} \tau^{c,tri}_A (\varepsilon^{n,tri}_1, \varepsilon^{n,tri}_2, \varepsilon^{n,tri}_3) P^A_{n,tri} .$$  

(57)

Using the condition that all of $\varepsilon^{n,tri}, \Delta \varepsilon$ and $\varepsilon^n$ share the same eigenbasis $P^A_{n,tri}$, the equation $\varepsilon^n = \varepsilon^{n,tri} - \Delta \varepsilon$ can be presented in the principal components as $\varepsilon^n_{A} = \varepsilon^{n,tri}_A - \delta_{AB} \Delta \tau^c_A (\varepsilon^n_{1}, \varepsilon^n_{2}, \varepsilon^n_{3}) \gamma$, where $\delta^{AB} = \delta_{AB} - 1/3$. Now, using the notation

$$\varepsilon^n = \begin{bmatrix} \varepsilon^n_{1} \\ \varepsilon^n_{2} \\ \varepsilon^n_{3} \end{bmatrix}, \quad \varepsilon^{n,tri} = \begin{bmatrix} \varepsilon^{n,tri}_{1} \\ \varepsilon^{n,tri}_{2} \\ \varepsilon^{n,tri}_{3} \end{bmatrix}, \quad \mathbb{I} = \frac{1}{3} \begin{bmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{bmatrix}$$

and

$$T^c(\varepsilon^n) = \begin{bmatrix} \tau^c_{11} \\ \tau^c_{22} \\ \tau^c_{33} \end{bmatrix},$$

(59)

one obtains the following residuum in vector form in principal components

$$r(\varepsilon^n) = \varepsilon^n - \varepsilon^{n,tri} + \frac{\Delta t}{\gamma(\varepsilon^n)} \mathbb{I} \cdot T^c(\varepsilon^n) = 0 .$$  

(60)

Eq. (60) is nonlinear in $\varepsilon^n$ and for its solution a Newton-Raphson scheme is devised where the details are given in Appendix D.2.

3.2.1. Derivation of the consistent inelastic moduli for the conformational stress $d\tau^c/d\varepsilon^{n,tri}$

In the derivation of the tangent stiffness matrix for the conformational stress which uses an elastic predictor-inelastic corrector type algorithm, we use the identity $d/d\varepsilon \equiv d/d\varepsilon^{n,tri}$. To this end, the residuum equation of the inelastic correction step is differentiated at the converged state resulting from the identity

$$dr = \frac{\partial r}{\partial \varepsilon^n} \cdot d\varepsilon^n + \frac{\partial r}{\partial \varepsilon^{n,tri}} \cdot d\varepsilon^{n,tri} = 0 .$$  

(61)

The partial derivatives in Eq. (61) are given as

$$\frac{\partial r}{\partial \varepsilon^n} = k \quad \text{and} \quad \frac{\partial r}{\partial \varepsilon^{n,tri}} = -1 ,$$

(62)

where $k$ is computed during local iterations using Eq. (D.14) and a rearrangement of Eq. (61) leads to

$$d\varepsilon^n = k^{-1} \cdot d\varepsilon^{n,tri} .$$  

(63)

This provides the tangent relations between the system variable $\varepsilon^n$ and the system input $\varepsilon^{n,tri}$. The consistent tangent operator for the conformational stress is obtained by differentiating the stress update formula which gives

$$dT^c = \frac{\partial T^c}{\partial \varepsilon^n} \cdot d\varepsilon^n .$$  

(64)
In view of Eq. (63) we reach
\[
d\mathbf{T}^c \over d\mathbf{e}^{n,\text{tri}} = q : \mathbf{e}^{-1},
\] (65)

where the components of \(q\) are computed during local iterations with \(q_{AB} = \partial \tau_{cA}^e / \partial \mathbf{e}_{AB}^b = \partial \tau_{cA}^e / \partial \mathbf{e}_{AB}^b\) with no summation over \(B\) along with Eqs. from (D.18) to (D.21) and (D.17). This is a tangent in principal components and the components of the matrix \(d\mathbf{T}^c / d\mathbf{e}^{n,\text{tri}}\) are in fact \(d\tau_{A}^c / d\mathbf{e}_{B}^{n,\text{tri}}\). To recover the total form \(d\tau^c / d\mathbf{e}^{n,\text{tri}}\) from the principal components \(d\tau_{A}^c / d\mathbf{e}_{B}^{n,\text{tri}}\) we start with the following notation

\[
\tau^c = p(e^n) = \sum_{A=1}^{3} \tau_A^c P_A^e \quad \text{and} \quad \mathbf{e}^{n,\text{tri}} = \sum_{A=1}^{3} \mathbf{e}_{A}^{n,\text{tri}} \mathbf{P}_A^{e,n,\text{tri}}.
\] (66)

Making use of elastic isotropy giving \(R_A = M_A \otimes M_A = P_A^e \otimes N_A^e = N_A^e \otimes N_A^e = P_A^{e,n,\text{tri}}\) and computing the spin tensor of the Lagrangian triad \(M_A = \sum_{B=1}^{3} W_{AB} M_B\) one obtains

\[
\dot{\tau}^c = \sum_{A=1}^{3} \frac{d\tau_{A}^c}{d\mathbf{e}^{n,\text{tri}}} \mathbf{M}_A \otimes M_A + \sum_{A,B=1, A \neq B}^{3} W_{AB} [\tau_B^c - \tau_A^c] [M_A \otimes M_B],
\] (67)

\[
\mathbf{e}^{n,\text{tri}} = \sum_{A=1}^{3} \mathbf{e}_{A}^{n,\text{tri}} \mathbf{M}_A \otimes M_A + \sum_{A,B=1, A \neq B}^{3} W_{AB} [\mathbf{e}_{A}^{n,\text{tri}} - \mathbf{e}_{B}^{n,\text{tri}}] [M_A \otimes M_B].
\] (68)

Using \(\dot{\tau}^c = d\tau^c / d\mathbf{e}^{n,\text{tri}}\), one deduces\(^4\) that

\[
\frac{d\tau^c}{d\mathbf{e}^{n,\text{tri}}} = \sum_{A,B=1}^{3} \frac{d\tau_{A}^c}{d\mathbf{e}^{n,\text{tri}}} M_A \otimes M_A \otimes M_B \otimes M_B
\]

\[+ \frac{1}{2} \sum_{A,B=1, A \neq B}^{3} \frac{[\tau_A^c - \tau_B^c]}{[\mathbf{e}_{A}^{n,\text{tri}} - \mathbf{e}_{B}^{n,\text{tri}}]} [M_A \otimes M_B \otimes M_A \otimes M_B + M_A \otimes M_B \otimes M_B \otimes M_A].
\] (69)

Algorithm 3 summarizes the procedure to obtain the conformational stress \(\tau^c\) and the corresponding tangent \(d\tau^c / d\mathbf{e}\).

**Algorithm 3** Computation of conformational stress \(\tau^c\) and conformational tangent \(d\tau^c / d\mathbf{e}\)

1. Input arguments: \(\Delta t, \epsilon_n, \Theta, \text{internal variables } I_n\).
2. Given material properties: \(\gamma^*, C^e, \Theta^\infty, \Theta^*, \alpha, \eta, N^e, k^b\).
3. Estimate trial state: \(\epsilon_{n,\text{tri}} = \epsilon_n^A + \Delta \epsilon\), where \(\Delta \epsilon = \epsilon - \epsilon_n\).
4. Calculate principal trial network stretch \(\lambda_{A}^{n,\text{tri}}\).
5. Calculate principal trial conformational stress \(\tau_{A}^{c,\text{tri}}\) using Eq. (20).
6. Calculate entanglement slippage \(\gamma\) using Eq. (22) and Eq. (23).
7. Compute residuum \(\mathbf{r}\) using Eq. (60).
8. Calculate updated network strains: \(\epsilon_{A,i+1}^n = \epsilon_{A,i}^n + \Delta \epsilon_{A}^n\) using Eq. (D.8).
9. **IF** \(|\mathbf{r}| < \text{TOL} \quad \text{CONTINUE}
10. Otherwise Go To step 4
11. Calculate principal network stretch \(\lambda_{A}^{n}\).
12. Calculate tangent \(d\tau^c / d\mathbf{e}^{n,\text{tri}}\) using Eqs. (69) and (65).
13. **RETURN** \(\tau^c, \epsilon_n^A\) and \(d\tau^c / d\mathbf{e}^{n,\text{tri}}\).
4. Application problem: axisymmetric blow molding of an amorphous polymer

To illustrate this formulation’s capability of handling large strain problems, a finite element simulation of an injection stretch-blow molding (ISBM) - a popular industrial process used in plastic bottle formation - is carried out, see simulations in e.g. [38–43]. The ISBM process consists of two distinct stages: (1) stretching - where the punch moves axially in the direction of the die to stretch the specimen, and (2) blowing - where air is blown through the cavity applying pressure on the specimen to obtain the desired shape of the die. In order to test the formulation presented in the current work, we take an ISBM setup containing a punch, a die and a specimen, as shown in Figure 2.

4.1. Finite element model

The geometry is discretized by finite elements of type CAX4 in Abaqus with five elements in thickness direction. The die and the punch are modeled as rigid bodies whereas the specimen is deformable. Surface-to-surface contact is created between punch–specimen and specimen–die contact surfaces, where the specimen is the slave surface in both cases. The interaction property between the punch–specimen surfaces are assigned a tangential frictionless behavior, whereas the specimen–die surfaces are assigned a contact where contact pressure only exists if the surfaces are in contact (referred as normal (hard contact) in Abaqus). The material properties are listed in Table A.1. Similar to the actual production process, we also use two steps to obtain the final desired shape. In the first step, the punch moves axially with a velocity of 1 mm/s, allowing the specimen to only stretch in the axial direction. In the second step, the punch is fixed and a pressure is applied to the internal surface of the specimen to obtain the final shape. In both steps, the die is not allowed to move and the temperature is set constant to 92°C. Figure 2 shows the injection stretch-blow molding process at various stages during the simulation.
4.2. Results

Since the purpose of this simulation is to demonstrate the capability and robustness of this formulation for analyzing real engineering problems, some basic results are shown here. Figure 3 shows the von Mises stress distribution in the specimen at various stages of the process.

![Figure 3: Von Mises stress distribution at various stages of the injection stretch-blow molding simulation.](image)

It is worth mentioning that no localized deformation in the form of necking is observed during the simulation. Even at the critical regions such as the neck as well as the bottom of the bottle, both of which have the potential of showing high deviation in thickness [38], we obtain a relatively uniform thickness distribution of $0.6 \pm 0.05$ mm. Since the bonding and conformational parts are stored separately as solution-dependent variables, we can monitor the individual contributions at the various stages of the simulation. In order to observe the cumulative effect of these contributions, we compute a von Mises-type bonding and conformational stress. Figures 4 and 5 depict the bonding and conformational von Mises stress contribution to the total stress, respectively. This allows one to individually observe the evolution of bonding and conformational stress throughout the process. The evolution of bonding stress in Figure 4 shows an increase up to the yield point, after which the bonding stress starts to decrease until the end of the process - a typical behavior of the bonding contribution. In contrast, the conformational stress in Figure 5 shows a continuous increase until the end of the process, signifying the strain hardening.

![Figure 4: Bonding von Mises stress contribution at various stages of the injection stretch-blow molding simulation.](image)
5. Conclusion

The kinematic assumption, on which the existing implementations of the glass-rubber constitutive model of Buckley and Jones [1] and its variants the more general rotational deformations, see, e.g., [3, 4] rely on, is based on the additivity of the rate of deformation tensor. This, in turn, results in a hypoelastic characterization of the bonding stress, a condition necessitating an appropriate objective time derivative selected on an ad hoc basis. In this work, following the footsteps of the work of Miehe et al. [17], we reformulate the constitutive model in Lagrangian logarithmic strain space. This not only hinders the need for hypoelastic characterization of the elastic response, which is found to be fundamentally objectionable [24–27], but also provides an implementation analogous to the corresponding geometrical linear theory. Algorithms for stress update as well as consistent tangent moduli computations are developed where significant size reductions in terms of the nonlinear equation sets for bonding and conformational parts, making up the glass-rubber constitutive model, are accomplished. These are implemented as a user-defined material subroutine (UMAT) in ABAQUS. Numerous verification studies and application problems, including constant-width tension, equi-biaxial tension, and simple shear tests as well as an injection stretch-blow molding process are presented where the last one demonstrates the capability of this reformulation for solving large strain problems of industrial interest.
Appendix A. Extended applications and verification of the implementation

Appendix A.1. Constant-width tension, equi-biaxial tension and simple shear loading of PET

Buckley et al. presented the glass-rubber constitutive model [1, 5] for PET. Adams et al. [2] extended the model for the same material and extracted various material parameters. Using this material data, ABAQUS is used to model the constitutive response with the help of a user-defined material model (UMAT) subroutine based on the algorithms introduced in Section 3. To characterize the material behavior numerically, a three-dimensional single-element is subjected to a constant-width tension\(^5\), equi-biaxial tension, and simple shear loading at appropriate conditions as used by Adams et al. [2].

Figure A.6 shows the typical behavior of PET corresponding to Adams et al. [2] work for constant-width tension and equi-biaxial tension of amorphous PET film at an extension rate of \(1 \text{s}^{-1}\) and at a temperature of 86°C. The stress-strain behavior for constant-width tension, and equi-biaxial tension matches with the published results of Adams et al. [2], indicating that the implementation of the constitutive equations is correct. The simple shear case is created to check the behavior of the algorithms when only shear components are activated. As mentioned previously, Dooling et al. [3] used a pseudo-linear solution method whereas in the current treatment all nonlinearity sources are considered in the local iteration schemes. In these solutions, the time increment is kept constant at 0.001 s. The used material parameters are summarized in Table A.1.

Table A.1: Parameters for the PET film required for the glass-rubber constitutive model, partly taken from Adams et al. [2].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Magnitude</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>General gas constant</td>
<td>(R)</td>
<td>8.3144621</td>
<td>J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>(k^b)</td>
<td>1.3806488 \times 10^{-23}</td>
<td>J K(^{-1})</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>(G^b)</td>
<td>600 \times 10^6</td>
<td>Pa</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>(\kappa)</td>
<td>1800 \times 10^6</td>
<td>Pa</td>
</tr>
<tr>
<td>Reference viscosity</td>
<td>(\mu^*)</td>
<td>19.7 \times 10^6</td>
<td>Pa s</td>
</tr>
<tr>
<td>Viscosity constant</td>
<td>(C)</td>
<td>439</td>
<td>K</td>
</tr>
<tr>
<td>Activation enthalpy</td>
<td>(\Delta H_0)</td>
<td>123 \times 10^3</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>Shear activation volume</td>
<td>(V^s)</td>
<td>7.23 \times 10^{-3}</td>
<td>m(^3) mol(^{-1})</td>
</tr>
<tr>
<td>Pressure activation volume</td>
<td>(V^p)</td>
<td>1.35 \times 10^{-3}</td>
<td>m(^3) mol(^{-1})</td>
</tr>
<tr>
<td>Entanglement density</td>
<td>(N^s)</td>
<td>2.75 \times 10^{26}</td>
<td>m(^{-3})</td>
</tr>
<tr>
<td>Reference slippage viscosity</td>
<td>(\gamma^*)</td>
<td>6.13 \times 10^6</td>
<td>Pa</td>
</tr>
<tr>
<td>Slippage viscosity constant</td>
<td>(C^s)</td>
<td>260</td>
<td>K</td>
</tr>
<tr>
<td>Reference temperature</td>
<td>(\Theta^*)</td>
<td>360.15</td>
<td>K</td>
</tr>
<tr>
<td>Limiting temperature</td>
<td>(\Theta^\infty)</td>
<td>329.15</td>
<td>K</td>
</tr>
<tr>
<td>Inextensibility factor</td>
<td>(\alpha)</td>
<td>0.164</td>
<td>–</td>
</tr>
<tr>
<td>Looseness of the entanglement(^6)</td>
<td>(\eta)</td>
<td>0</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^5\)Constant-width tension is also referred to as pure shear e.g. [44], however, we are using the term for consistency with the works by Buckley et al. [1, 5] and Adams et al. [2].

\(^6\)Eq. (14) is based on a theory provided by Edwards et al. [30, 31], which is generally for a crosslinked, entangled polymers. However, Adams et al. [2] considered a limiting case of an uncrosslinked polymer i.e. the density of crosslink vanishes with respect to the density of entanglements. For such a case, slip-link axial mobility factor (or looseness of the entanglement), \(\eta\), is set to zero for a crosslink.
Figure A.6: Stress-strain curves for constant-width tension, equi-biaxial tension, and simple shear loading of PET at a constant strain rate of $1 \text{s}^{-1}$ and at a temperature of $86 \degree \text{C}$. The points shown represent the FE nodes where loading and boundary conditions are applied. The arrow shows the direction of the applied loading, while the remaining degrees of freedom are fixed. The nominal strain for (a) is $\epsilon_{11} = F_{11} - 1$, for (b) is $\epsilon_{11} = \epsilon_{22} = F_{11} - 1 = F_{22} - 1$, for (c) is $\epsilon_{12} = \frac{1}{2} F_{12}$, where 1, 2 and 3 stand for the x, y and z axis, respectively.

**Appendix A.2. Convergence study**

Since the algorithms used in this formulation are based on Newton-Raphson iterative scheme, with a correct linearization a quadratic convergence is anticipated around the solution. Typical convergence behaviors observed for the bonding and conformational part using this algorithm at two selected time steps (at the beginning and final stages of deformation) during the constant-width tension, equi-biaxial tension,
and simple shear loading simulations are illustrated in Table A.2, A.3 and A.4, respectively. Indeed, a quadratic convergence is observed, which corroborates the implemented Newton-Raphson scheme.

<table>
<thead>
<tr>
<th>Time Step / Strain</th>
<th>Iteration</th>
<th>Residuum Bonding</th>
<th>Conformational Bonding</th>
<th>Conformational Converged σ11 stress [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 / 0.01</td>
<td>0</td>
<td>7.4409 x 10^-04</td>
<td>7.0722 x 10^-07</td>
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</tr>
<tr>
<td></td>
<td>1</td>
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<td>1.2791 x 10^-17</td>
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</tr>
<tr>
<td></td>
<td>2</td>
<td>1.6335 x 10^-04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.2860 x 10^-09</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.4409 x 10^-16</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2000 / 2.0</td>
<td>0</td>
<td>2.9845 x 10^-01</td>
<td>1.1213 x 10^-04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
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<td>1.5757 x 10^-12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.1731 x 10^-06</td>
<td>9.2435 x 10^-17</td>
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</tr>
<tr>
<td></td>
<td>3</td>
<td>2.9710 x 10^-13</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table A.3: Convergence behavior of the algorithm of the equi-biaxial tension test of a single-element corresponding to Figure A.6(b).

<table>
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<tr>
<th>Time Step / Strain</th>
<th>Iteration</th>
<th>Residuum Bonding</th>
<th>Conformational Bonding</th>
<th>Conformational Converged σ11 stress [MPa]</th>
</tr>
</thead>
<tbody>
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<td>3.2934 x 10^-04</td>
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</tr>
<tr>
<td></td>
<td>1</td>
<td>4.5981 x 10^-07</td>
<td>9.8891 x 10^-12</td>
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</tr>
<tr>
<td></td>
<td>2</td>
<td>8.4377 x 10^-15</td>
<td>1.0085 x 10^-17</td>
<td></td>
</tr>
<tr>
<td>2000 / 2.0</td>
<td>0</td>
<td>2.3029 x 10^-04</td>
<td>6.5207 x 10^-04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.1868 x 10^-09</td>
<td>2.0029 x 10^-07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.2205 x 10^-16</td>
<td>6.1488 x 10^-11</td>
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<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>1.8750 x 10^-14</td>
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Table A.4: Convergence behavior of the algorithm of the simple shear test of a single-element corresponding to Figure A.6(c).

<table>
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<th>Time Step / Strain</th>
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<th>Conformational Bonding</th>
<th>Conformational Converged σ11 stress [MPa]</th>
</tr>
</thead>
<tbody>
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<td>4.0807 x 10^-04</td>
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<td>6.5696 x 10^-03</td>
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<tr>
<td></td>
<td>2</td>
<td>2.0303 x 10^-06</td>
<td>-</td>
<td></td>
</tr>
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<td></td>
<td>3</td>
<td>1.9274 x 10^-13</td>
<td>-</td>
<td></td>
</tr>
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<td>2000 / 2.0</td>
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</tr>
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<td>1.2468 x 10^-02</td>
<td>4.8673 x 10^-14</td>
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<td>2</td>
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<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.3978 x 10^-11</td>
<td>-</td>
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</tr>
<tr>
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<td>4</td>
<td>8.8818 x 10^-16</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Appendix A.3. Comparison of analytical and numerical tangent moduli
As mentioned earlier, the tangent moduli have been computed both analytically and numerically. The latter proves useful in verification of the derivations and the implementation of the analytical tangent
especially for complex material models. Tables A.5 and A.6 demonstrate comparisons between the two tangent moduli for the constant-width tension and simple shear tests, respectively, computed at the final load step. For each test, the tangent moduli for both bonding and conformational parts are shown separately and the relative differences are calculated. It can be observed that the difference is considerably small for both loading cases, which corroborates the derived and implemented analytical tangent computations.

Table A.5: Comparison between numerical and analytical tangent moduli for the constant-width tension test in terms of relative difference. For this test, we set $V^s = V^p = 1000$ mm$^3$ mol$^{-1}$, to reduce the sensitivity of numerical tangent to the applied perturbations at the observed level of deformation.

<table>
<thead>
<tr>
<th></th>
<th>Analytical tangent</th>
<th>Numerical tangent</th>
<th>Relative difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_{1111}$</td>
<td>$c_{1111}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2.3484948037 \times 10^{+03}$</td>
<td>$2.3471410512 \times 10^{+03}$</td>
<td>$5.7643 \times 10^{-02}$</td>
</tr>
<tr>
<td></td>
<td>$c_{2222}$</td>
<td>$c_{2222}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2.3839807656 \times 10^{+03}$</td>
<td>$2.385336784 \times 10^{+03}$</td>
<td>$5.6750 \times 10^{-02}$</td>
</tr>
<tr>
<td></td>
<td>$c_{3333}$</td>
<td>$c_{3333}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2.3661938261 \times 10^{+03}$</td>
<td>$2.3661936441 \times 10^{+03}$</td>
<td>$7.6886 \times 10^{-06}$</td>
</tr>
<tr>
<td></td>
<td>$c_{1212}$</td>
<td>$c_{1212}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.5468434018 \times 10^{+02}$</td>
<td>$1.546843018 \times 10^{+02}$</td>
<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{1313}$</td>
<td>$c_{1313}$</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>$3.1877257861 \times 10^{+02}$</td>
<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{2323}$</td>
<td>$c_{2323}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3.2841683366 \times 10^{+02}$</td>
<td>$3.2841683366 \times 10^{+02}$</td>
<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{1122}$</td>
<td>$c_{1122}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.493020753 \times 10^{+03}$</td>
<td>$1.4916672068 \times 10^{+03}$</td>
<td>$9.0660 \times 10^{-02}$</td>
</tr>
<tr>
<td></td>
<td>$c_{1133}$</td>
<td>$c_{1133}$</td>
<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>$c_{2233}$</td>
<td>$c_{2233}$</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>$1.493479845 \times 10^{+03}$</td>
<td>$9.0706 \times 10^{-02}$</td>
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</tbody>
</table>

Table: Analytical tangent Numerical tangent Relative difference [%]

<table>
<thead>
<tr>
<th></th>
<th>Analytical tangent</th>
<th>Numerical tangent</th>
<th>Relative difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_{1111}$</td>
<td>$c_{1111}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4.5581367432 \times 10^{+01}$</td>
<td>$4.5581366971 \times 10^{+01}$</td>
<td>$1.0106 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{2222}$</td>
<td>$c_{2222}$</td>
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</tr>
<tr>
<td></td>
<td>$3.2489781355 \times 10^{+03}$</td>
<td>$3.2489121685 \times 10^{+03}$</td>
<td>$2.0304 \times 10^{+03}$</td>
</tr>
<tr>
<td></td>
<td>$c_{3333}$</td>
<td>$c_{3333}$</td>
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</tr>
<tr>
<td></td>
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<td>$5.4227589512 \times 10^{-01}$</td>
<td>$4.8051 \times 10^{-05}$</td>
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<tr>
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<td>$c_{1212}$</td>
<td>$c_{1212}$</td>
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</tr>
<tr>
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<td>$1.5270086688 \times 10^{-01}$</td>
<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{1313}$</td>
<td>$c_{1313}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2.8141253761 \times 10^{-01}$</td>
<td>$2.8141253761 \times 10^{-01}$</td>
<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
<td></td>
<td>$c_{2323}$</td>
<td>$c_{2323}$</td>
<td></td>
</tr>
<tr>
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<td>$0.0000 \times 10^{+00}$</td>
</tr>
<tr>
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<td>$c_{1122}$</td>
<td></td>
</tr>
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<td>$c_{1133}$</td>
<td></td>
</tr>
<tr>
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<td>$c_{2233}$</td>
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</tr>
<tr>
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<td>$4.1974268505 \times 10^{-02}$</td>
<td>$6.9913 \times 10^{-05}$</td>
</tr>
</tbody>
</table>
Similarly, if $\epsilon = V^t V = 1000 \text{mm}^3 \text{mol}^{-1}$, to reduce the sensitivity of numerical tangent to the applied perturbations at the observed level of deformation.

For this test, we set $p = 1000$ mm.

### Table A.6: Comparison between numerical and analytical tangent moduli for the simple shear test in terms of relative difference.

<table>
<thead>
<tr>
<th></th>
<th>Analytical tangent</th>
<th>Numerical tangent</th>
<th>Relative difference [%]</th>
</tr>
</thead>
<tbody>
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<td>Bonding</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>$2.4005645923 \times 10^{-03}$</td>
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</tr>
<tr>
<td>$c_{3333}$</td>
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<td>$2.338651054 \times 10^{-03}$</td>
<td>$3.0317 \times 10^{-02}$</td>
</tr>
<tr>
<td>$c_{1212}$</td>
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<td>$3.5879896616 \times 10^{-02}$</td>
<td>$0.0000 \times 10^{00}$</td>
</tr>
<tr>
<td>$c_{1313}$</td>
<td>$2.7971218969 \times 10^{-02}$</td>
<td>$2.7971264537 \times 10^{-02}$</td>
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</tr>
<tr>
<td>$c_{2323}$</td>
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<td>$3.6345703731 \times 10^{-02}$</td>
<td>$0.0000 \times 10^{00}$</td>
</tr>
<tr>
<td>$c_{1122}$</td>
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<td>$1.5005308469 \times 10^{-03}$</td>
<td>$4.7318 \times 10^{-02}$</td>
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</tr>
<tr>
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<td>$1.5012423552 \times 10^{-03}$</td>
<td>$7.7069 \times 10^{-05}$</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>$c_{3333}$</td>
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<td>$c_{1212}$</td>
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<td>$0.0000 \times 10^{00}$</td>
</tr>
<tr>
<td>$c_{1313}$</td>
<td>$9.4233411087 \times 10^{-01}$</td>
<td>$9.4233439797 \times 10^{-01}$</td>
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</tr>
<tr>
<td>$c_{2323}$</td>
<td>$-3.5079629041 \times 10^{-02}$</td>
<td>$-3.5079629041 \times 10^{-02}$</td>
<td>$0.0000 \times 10^{00}$</td>
</tr>
<tr>
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</tr>
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<td>$8.7029214581 \times 10^{-01}$</td>
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</tr>
<tr>
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<td>$2.304589082 \times 10^{-01}$</td>
<td>$8.3222 \times 10^{-05}$</td>
</tr>
</tbody>
</table>

### Appendix A.4. Robustness of implementation: Hypothetical loading cases

To test the robustness of the UMAT implementation, a three-dimensional multi-element cube is subjected to two extreme loading conditions. In the first scenario, the cube is subjected to a uniaxial tensile loading while in the second scenario, it is subjected to a combined tensile and torsion loading. In both cases, all degrees of freedom are restricted on one side of the cube and the opposite side is accordingly loaded at an engineering strain rate of $1 \text{ s}^{-1}$ at $86^\circ \text{C}$. A fixed time increment of 0.1 s is selected.

Figures A.7 and A.8 depict the cube under tensile and a combined tensile and torsion loading, respectively, in terms of von Mises stress distribution, where $\epsilon$ denotes the axial strain and $n$ the number of turns. In the combined tensile and torsion loading, for every axial strain of 30%, a quarter turn is made. In both examples, the solution converges robustly and is obtained in 100 load steps. The average number of global iterations for uniaxial tensile and combined tensile and torsion loading is 4 and 5, respectively.

### Appendix B. l’Hospital rule

In the particular case if $\lambda_A = \lambda_B$, Eq. (44) has $f' (\lambda^2_A) = f' (\lambda^2_B)$ and Eq. (45) has $h' (\lambda^2_A) = h' (\lambda^2_B)$. The quotient in these expressions can be evaluated using l’Hospital rule to give

$$\lim_{\lambda_B \rightarrow \lambda_A} \frac{f (\lambda^2_A) - f (\lambda^2_B)}{\lambda^2_A - \lambda^2_B} = f' (\lambda^2_B) = -\frac{1}{2\lambda^4_B},$$  \hspace{1cm} (B.1)$$

and

$$\lim_{\lambda_B \rightarrow \lambda_A} \frac{h (\lambda^2_A) - h (\lambda^2_B)}{\lambda^2_A - \lambda^2_B} = h' (\lambda^2_B) = \frac{1}{2\lambda^2_B}.$$  \hspace{1cm} (B.2)$$

Similarly, if $\epsilon^{\text{tri}}_{\tau_A} = \epsilon^{\text{tri}}_{\tau_B}$ in Eq. (69), isotropy implies that $\tau^A_A = \tau^B_B$, and the quotient in the expression becomes
Appendix C. Numerical tangent

The numerical tangent can be computed using Algorithm 4.

\[
\lim_{\varepsilon_{n,\text{tri}} \to \varepsilon_{A,\text{tri}}} \frac{\tau_{A} - \tau_{B}}{\varepsilon_{A,\text{tri}} - \varepsilon_{B,\text{tri}}} = \frac{\partial \tau_{B}}{\partial \varepsilon_{B,\text{tri}}} - \frac{\partial \tau_{A}}{\partial \varepsilon_{B,\text{tri}}}
\]  

\[(B.3)\]
Algorithm 4 Computation of the numerical tangent [36].

1: Input arguments: $\mathbf{F}, \sigma$, internal variables $\mathcal{I}_n$.
2: For $(kl) = (11), (22), (33), (12), (13), (23)$, compute the following:

(a) perturbed deformation gradient, using an appropriate perturbation parameter $\iota$
$$\tilde{\mathbf{F}}^{(kl)}_{ij} = \mathbf{F}_{ij} + \frac{\iota}{2} [\delta_{ik} \mathbf{F}_{lj} + \delta_{il} \mathbf{F}_{kj}] .$$

(b) perturbed Cauchy stress
$$\tilde{\sigma}^{(kl)} = \tilde{\sigma}^{(kl)} \left( \tilde{\mathbf{F}}^{(k)}, \mathcal{I}_n \right) .$$

(c) column $(kl)$ for the spatial tangent corresponding to Eq. (39)
$$c_{ij}^{(kl)} = \frac{1}{\iota} \left[ \frac{\det \left( \tilde{\mathbf{F}}^{(k)} \right)}{\det (\mathbf{F})} \tilde{\sigma}^{(kl)}_{ij} - \sigma_{ij} \right] - \frac{1}{2} \left[ \delta_{ik} \sigma_{jl} + \delta_{il} \sigma_{jk} + \sigma_{ik} \delta_{jl} + \sigma_{il} \delta_{jk} \right] .$$

Appendix D. Auxiliary derivations

Appendix D.1. Bonding part

For the bonding part, Eq. (50) gives the residuum which is required to vanish for the solution. By using a Taylor series expansion around current state, identified by the index $i$ which also stands for the iteration counter, using $\tau_{i+1}^{\text{b,oct}} = \tau_{i}^{\text{b,oct}} + \Delta \tau_{b,\text{oct}}$ and canceling out higher-order terms, we obtain
$$0 = r(\tau_{i+1}^{\text{b,oct}}) \simeq r(\tau_{i}^{\text{b,oct}}) + \frac{\partial r}{\partial \tau_{b,\text{oct}}} \bigg|_{\tau_{b,\text{oct}}^{i}} \Delta \tau_{b,\text{oct}} ,$$
which gives the iterative increment
$$\Delta \tau_{b,\text{oct}} = - k^{-1} \bigg|_{\tau_{b,\text{oct}}^{i}} r(\tau_{i}^{\text{b,oct}}) ,$$
with $k := \partial r / \partial \tau_{b,\text{oct}}$ resulting in
$$k = 1 + \frac{\partial r}{\partial \mu} \frac{\partial \mu}{\partial \tau_{b,\text{oct}}} .$$
In the above expression, we can compute $\partial r / \partial \mu$ as
$$\frac{\partial r}{\partial \mu} = - \frac{2 \psi \Delta t}{[2 \psi \Delta t + \mu]^{2}} .$$
Considering Eq. (28), $\omega := \partial \mu / \partial \tau_{b,\text{oct}}$ is computed using the chain rule of differentiation to give
$$\omega = \frac{\partial \mu}{\partial \tau_{b,\text{oct}}} = \mu_0 \Omega \text{csch} (\Xi) [1 - \Xi \coth (\Xi)] \frac{V^s}{2R \Theta} .$$
By combining Eqs. (D.3), (D.4) and (D.5) we obtain
$$k = 1 - \omega \frac{2 \psi \Delta t}{[2 \psi \Delta t + \mu]^{2}} .$$
Appendix D.2. Conformational part

For the conformational part, Eq. (60) gives the residuum which is required to vanish for the solution. By using a Taylor series expansion around current state, identified by the index \( i \) which also stands for the iteration counter, using \( \varepsilon_{i+1} = \varepsilon_i + \Delta \varepsilon_i \) and canceling out higher-order terms, we obtain

\[
0 = r(\varepsilon_{i+1}) \simeq r(\varepsilon_i) + \frac{\partial r}{\partial \varepsilon_i} \Delta \varepsilon_i, \quad (D.7)
\]

which gives the iterative increment

\[
\Delta \varepsilon_i = -k^{-1} r(\varepsilon_i), \quad (D.8)
\]

with \( k := \partial r/\partial \varepsilon_i \) resulting in

\[
k = 1 + \frac{\partial r}{\partial \gamma} \otimes \frac{\partial \gamma}{\partial \varepsilon_i} + \frac{\partial r}{\partial \tau} T^c + \frac{\partial \tau}{\partial \varepsilon_i}, \quad (D.9)
\]

where \( 1 \) denotes the \( 3 \times 3 \) identity matrix. In Eq. (D.9), we compute the partial derivatives as

\[
\frac{\partial r}{\partial \tau} = \frac{\Delta t}{\gamma^2} \cdot T^c \quad \text{and} \quad \frac{\partial r}{\partial \tau} = \frac{\Delta t}{\gamma} \cdot \Gamma.
\]

Coming to \( \partial \gamma/\partial \varepsilon_i \), we have

\[
\frac{\partial \gamma}{\partial \varepsilon_i} = \frac{\partial \gamma}{\partial \lambda_{i,\max}} \frac{\partial \lambda_{i,\max}}{\partial \varepsilon_i}, \quad (D.10)
\]

with

\[
\frac{\partial \gamma}{\partial \lambda_{i,\max}} = \gamma_0 \frac{[\lambda_{\text{crit}} - 1]}{[\lambda_{\text{crit}} - \lambda_{i,\max}]^2} \quad \text{and} \quad \frac{\partial \lambda_{i,\max}}{\partial \varepsilon_i} = \frac{\partial \lambda_{i,\max}}{\partial \lambda_A} \lambda_A^i \quad \text{(no summation over} \ A). \quad (D.11)
\]

The expression \( \partial \lambda_{i,\max}/\partial \varepsilon_i \) results in the form \( \partial \lambda_{i,\max}/\partial \varepsilon_i = \lambda_{i,\max}^n t \) where considering repeating eigenvalues, vector \( t \) can have one of the following seven forms

\[
\left[ \begin{array}{llllll}
1 & 0 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 & 1 & 1 \\
0 & 0 & 1 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 1 & 1 & 1 \\
0 & 0 & 0 & 0 & 1 & 0
\end{array} \right]. \quad (D.12)
\]

Finally, using the notation \( q := \partial T^c/\partial \varepsilon_i \) and combining above findings, we obtain

\[
k = 1 - \gamma_0 \frac{\lambda_{i,\max} [\lambda_{\text{crit}} - 1]}{[\lambda_{\text{crit}} - \lambda_{i,\max}]^2} \frac{\Delta t}{\gamma^2} T^c \otimes \tau + \frac{\Delta t}{\gamma} \Delta \lambda_A \cdot q. \quad (D.13)
\]

The components \( q_{AB} \) are computed using \( q_{AB} = \partial \tau_A/\partial \varepsilon_i B = \partial \tau_A/\partial \lambda_A^B \lambda_B^i \) with no summation over \( B \). The expression for \( \tau_A^i \) is given in Eq. (20), which requires computation of \( \partial \Psi/\partial \lambda_A^i \) with application of the chain rule

\[
\frac{\partial \Psi}{\partial \lambda_A^i} = \frac{\partial \Psi}{\partial \xi} \frac{\partial \xi}{\partial \lambda_A^i} + \frac{\partial \Psi}{\partial \xi} \frac{\partial \xi}{\partial \phi} \frac{\partial \phi}{\partial \lambda_A^i}, \quad (D.14)
\]

where

\[
\frac{\partial \Psi}{\partial \xi} = D \left[ \frac{1}{\zeta} - E \frac{\xi}{\zeta^2} \right], \quad \frac{\partial \Psi}{\partial \xi} = DE \frac{1}{\zeta} \quad \text{and} \quad \frac{\partial \Psi}{\partial \phi} = D, \quad (D.15)
\]

and

\[
\frac{\partial \xi}{\partial \lambda_A^i} = -2 \lambda_A^i, \quad \frac{\partial \xi}{\partial \lambda_A^i} = \frac{2 \lambda_A^i}{[1 + \eta (\lambda_A^i)^2]^3} \quad \text{and} \quad \frac{\partial \phi}{\partial \lambda_A^i} = \frac{2 \eta \lambda_A^i}{[1 + \eta (\lambda_A^i)^2]^2}. \quad (D.16)
\]
The computation of the components $q_{AB}$ requires derivation of $\partial \tau^c_A / \partial \lambda^n_B$ with

$$\frac{\partial \tau^c_A}{\partial \lambda^n_B} = \frac{\partial \tau^c_A}{\partial \lambda^n_B} \bigg|_{\xi, \zeta \to \text{const.}} + \frac{\partial \tau^c_A}{\partial \xi} \frac{\partial \xi}{\partial \lambda^n_B} + \frac{\partial \tau^c_A}{\partial \zeta} \frac{\partial \zeta}{\partial \lambda^n_B}, \quad (D.18)$$

where

$$\frac{\partial \tau^c_A}{\partial \lambda^n_B} \bigg|_{\xi, \zeta \to \text{const.}} = \begin{cases} \chi & \text{if } A = B, \\ 0 & \text{if } A \neq B, \end{cases} \quad (D.19)$$

with

$$\chi = 4D\alpha^2\lambda^n_A \left[ E \frac{\xi}{\zeta^2} - \frac{1}{\zeta} \right] + D E \frac{4\lambda^n_A}{\zeta [1 + \eta(\lambda^n_A)^2]^3} + D \frac{2\eta\lambda^n_A}{[1 + \eta(\lambda^n_A)^2]^2}, \quad (D.20)$$

and

$$\frac{\partial \tau^c_A}{\partial \xi} = 2D\alpha^2|\lambda^n_A|^2 \frac{1}{\zeta^2} \quad \text{and} \quad \frac{\partial \tau^c_A}{\partial \zeta} = 2D\alpha^2|\lambda^n_A|^2 \left[ \frac{1}{\zeta^2} - 2E \frac{\xi}{\zeta^3} \right] - D E \frac{1}{\zeta^2} \frac{2|\lambda^n_A|^2}{[1 + \eta|\lambda^n_A|^2]^2}. \quad (D.21)$$
References


