SANDIA REPORT SAND2023-14317 Printed December 2023



Theory and Implementation of the Spectacular Nonlinear Viscoelastic Constitutive Model

Kenneth N. Cundiff (01558), Michael R. Buche (01558), Brandon Talamini (LLNL), Scott J. Grutzik (01558), Jamie M. Kropka (01853), Kevin N. Long (01558)

Prepared by Sandia National Laboratories Albuquerque, New Mexico 87185 Livermore, California 94550 Issued by Sandia National Laboratories, operated for the United States Department of Energy by National Technology & Engineering Solutions of Sandia, LLC.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy Office of Scientific and Technical Information P.O. Box 62 Oak Ridge, TN 37831

Telephone:	(865) 576-8401
Facsimile:	(865) 576-5728
E-Mail:	reports@osti.gov
Online ordering:	http://www.osti.gov/scitech

Available to the public from

U.S. Department of Commerce National Technical Information Service 5301 Shawnee Road Alexandria, VA 22312

Telephone:(800) 553-6847Facsimile:(703) 605-6900E-Mail:orders@ntis.govOnline order:https://classic.ntis.gov/help/order-methods



ABSTRACT

This report is a comprehensive guide to the nonlinear viscoelastic Spectacular model, which is an isotropic, thermo-rheologically simple constitutive model for glass-forming materials, such as amorphous polymers. Spectacular is intermediate in complexity to the previous PEC and SPEC models (Potential Energy Clock and Simplified Potential Energy Clock models, respectively). The model form consists of two parts: a Helmholtz free energy functional and a nonlinear material clock that controls the rate of viscoelastic relaxation. The Helmholtz free energy is derived from a series expansion about a reference state. Expressions for the stress and entropy functionals are derived from the Helmholtz free energy following the Rational Mechanics approach. The material clock depends on a simplified expression for the potential energy, which itself is a functional of the temperature and strain histories. This report describes the thermo-mechanical theory of Spectacular, the numerical methods for time-integrating the model, model verification for its implementation in LAMÉ, a user guide for its implementation in LAMÉ, and ideas for future work. A number of appendices provide supplementary mathematical details and a description of the procedure used to derive the simplified potential energy from the full expression for the potential energy. The goal of this report is create a convenient point-of-entry for engineers who wish to learn more about Spectacular, but also to serve as a reference manual for advanced users of the model.

ACKNOWLEDGEMENTS

Many thanks to Brenton Elisberg, Alyssa Skulborstad, and Brian Lester for reviewing the manuscript.

CONTENTS

Ex	ecutive summary	9
1.	Introduction1.1. Motivation1.2. Overview of material in this report1.3. Mathematical conventions	13 13 13 14
2.	Model theory2.1. Model summary2.2. Kinematics2.3. Helmholtz free energy2.4. Equilibrium and instantaneous viscoelastic limits2.5. Stress2.6. Clock definition2.7. Specification of the relaxation functions	17 17 17 18 19 21 22 26
3.	 Thermo-mechanical coupling 3.1. Introduction 3.2. Definition of a thermodynamic process 3.3. Thermodynamically consistent constitutive equations for materials with memory that relax on a material timescale 3.3.1. General theory 3.3.2. Constitutive equations for the Spectacular model 3.3.3. Auxiliary constitutive equations 3.4. Heat equation 3.5. Computing instantaneous heat capacities 	27 27 27 29 30 31 34 34 36
4.	Implementation4.1. Updating the hereditary integrals4.1.1. Single hereditary integrals4.1.2. Double hereditary integrals4.1.3. Single hereditary integrals with $\frac{\partial f_r(t^* - s^*)}{\partial t}$ as the kernel4.1.4. Double hereditary integrals with $\frac{\partial f_r(t^* - s^*)}{\partial t}$ as the kernel4.2. Newton-Raphson method4.2.1. Defining the residual function4.2.3. Derivative of the residual function	 39 39 39 41 42 43 44 44 45 45
5.	 Verification 5.1. Introduction 5.2. Shift factor during a stress-free cool-hold-reheat cycle 5.3. Using the Arrhenius Sub–Glass Transition Shift Factor to Predict the Equilibrium Yield Stress After Isothermal Aging 	47 47 47 49

	 5.4. Creep with strain hardening 5.5. Zero-strain cooling at a constant temperature rate 5.6. Conclusion 	51 53 59
6.	User guide	61
7.	Conclusion	69
Re	ferences	73
A.	Relating the tangent and secant coefficients of thermal expansion	77
B.	 Deriving the Spectacular clock from the PEC clock B.1. Expression for the potential energy used in the PEC clock B.2. Derivation of the simplified potential energy used in the Spectacular clock B.3. Method for comparing the Spectacular and PEC clocks 	79 79 81 82
C.	Leibniz Integral Rule for Differentiation Under the Integral SignC.1. Time-derivative of a single hereditary integralC.2. Time-derivative of a double hereditary integralC.3. Time derivative of a Prony integral	83 83 84 85
D.	Calibration for 828/DEA Used to Simulate Yield Stress Evolution After Isothermal Aging	87
E.	Calibration for 828/DEA Used to Simulate Creep	91
Dis	stribution	95

LIST OF FIGURES

Figure 2-1.	The WLF equation, the Arrhenius equation, and the piecewise shift factor func-	
	tion used by Spectacular, Eq. (2.43). $C_1 = 10, C_2 = 50 \text{ K}, \theta_{\text{ref}} = 100 ^{\circ}\text{C}, N_{\text{match}} =$	
	$85 ^{\circ}\text{C}$, $A_2 = 20000\text{K}$. A_1 is calculated according to Eq. (2.44) to ensure the two	
	pieces of the function join at <i>N</i> _{match}	23
Figure 5-1.	(a) Verification of the shift factor as a function of the clock temperature, $\log a(N)$,	
	which is given by Eq. (2.43). (b) Verification of the equilibrium shift factor as	
	a function of temperature, $\log a_{\infty}(\theta)$, which is given by Eq. (2.50). Parameters	
	for the calculations are listed in Table 5-1	49
Figure 5-2.	Demonstration of converting from shift factor expressed as a function of tem-	
	perature to the equilibrium shift factor expressed as a function of $N_{\infty}(\theta)$. The	
	expression for $\log \hat{a}(\theta)$ is shown in Eq. (2.48) and the expression for $\log a_{\infty}(\theta) =$	
	$\log a(N_{\infty}(\theta))$ is shown in Eq. (2.50)	50

Figure 5-3.	Compressive yield stress after isothermal aging of 828/DEA for experiments (triangles) and Spectacular predictions (squares). (a) Predictions using the pa-	
	rameters given in Table 5-5 of Ref. [1]. (b) Predictions that modify the parame-	
	ters from Table 5-5 of Ref. [1] to utilize the Arrhenius sub–glass transition shift	
	factor with $E_a/R = 15000$ K and $\theta_{\text{match}} = 71^{\circ}$ C	51
Figure 5-4.	Predictions for creep in tension and compression without strain hardening	52
Figure 5-5.	Effect of increasing the strain hardening parameter $G^{I_2}_{\infty}$ on the tensile creep re-	
	sponse at 14 MPa.	52
Figure 5-6.	Temperature and volume strain histories applied for the zero-strain cooling at	
	constant temperature rate verification problem.	53
Figure 5-7.	Verification of the Helmholtz free energy and its partial derivatives during zero-	
	strain cooling at a constant temperature rate. Parameters for the calculations are	
	listed in Table 5-2.	57
Figure 5-8.	Verification of the terms in the heat equation during zero-strain cooling at a	
-	constant temperature rate. Parameters for the calculations are listed in Table 5-2.	58
Figure 5-9.	Verification of the potential energy and clock temperature during zero-strain	
C	cooling at a constant temperature rate. Parameters for the calculations are listed	
	in Table 5-2.	58

LIST OF TABLES

Table 3-1.	State variables for calculating heat capacities	38
Table 5-1.	Parameters used to verify the piecewise shift factor function under a stress-free	
	cool-hold-heat cycle. Unlisted parameters are either irrelevant to this thermo-	
	mechanical history, assume their default value, or are zero	48
Table 5-2.	Parameters used for the verification problem of zero-strain cooling at a con-	
	stant temperature rate. Unlisted parameters are either irrelevant to the thermo-	
	mechanical history, assume their default value, or are zero	54
Table 6-1.	State variables for the Spectacular model. Thermodynamic quantities	64
Table 6-2.	State variables for the Spectacular model. Hereditary integrals	65
Table 6-3.	State variables for the Spectacular model. Hereditary integrals with $\partial f_r(t^*)/\partial t$	
	kernels.	66
Table 6-4.	State variables for the Spectacular model. Hereditary integrals on single Prony	
	terms	67

EXECUTIVE SUMMARY

Fiscal year 2023 developments are summarized here with references to the sections, figures, and equations that fully describe the recent model changes.

Addition of a non-diverging shift factor that transitions from WLF to Arrhenius. A new option for the shift factor was added. Previously, the shift factor used a WLF form. Now, the shift factor can also be defined as a piecewise function that is WLF in the rubbery state and Arrhenius in the glassy state, see Eq. (2.43). Unlike the WLF equation, the Arrhenius equation does not diverge for positive values, and is consistent with the equilibrium sub-glass transition shift factor measured in experiments on amber aged for 20-million years [2]. Proper implementation of the piecewise shift factor is demonstrated in Fig. 5-1. In the model, the shift factor is a function of the state variable N, which is a proxy for the simplified potential energy, but has units of temperature. For convenience, the user can instead define the equilibrium shift factor as a function of temperature. The temperature form for the shift factor is shown in Eq. (2.48). Internally, the model will approximately convert the temperature-based parameters to the *N*-based parameters using Eqs. (2.51) to (2.53) and (2.55). Demonstration of the conversion from the temperature-based shift factor equation to the *N*-based shift factor equation is shown in Fig. 5-2. Previously, the diverging form of the WLF-only shift factor caused the yield stress to age far beyond experimental measurements [3]. Figure 5-3 demonstrates that this issue can be addressed using the new non-diverging shift factor.

Addition of isotropic strain hardening through strain-dependent bulk and shear moduli.

Isotropic strain hardening was added to the model following one of the approaches discussed in SAND2020-0160CTF [4]. Polymers exhibit large-strain hardening, which can arrest instabilities that begin from post-yield softening. If a constitutive model does not include strain hardening, then not only can the model not predict the large-strain behavior of many polymers, but instabilities from softening can lead to non-convergence of finite element models. In Spectacular, strain hardening was implemented by allowing the bulk and shear modulus, both glassy and rubbery, to depend on strain. To maintain the isotropic nature of Spectacular, the moduli depend linearly on the three generic invariants of the strain; see Eqs. (2.13), (2.14), (2.17) and (2.18). This dependence of the moduli on strain gives rise to second-order integral terms in the stress equation; see Eq. (2.39). The prefactors for these second-order integrals involve derivatives of the moduli with respect to strain; see Eqs. (2.24) to (2.26) and (2.30). Figure 5-5 shows that the strain hardening terms allow the model to predict stable tensile creep.

Modification of the equilibrium heat capacity terms. The original PEC model [5, 6] was a full thermo-mechanical description of a viscoelastic material, and therefore included thermal terms. These thermal terms were removed as part of the simplification from PEC to SPEC [7]. Thermal terms were added back into Spectacular in 2019 according to SAND2019-12917CTF [8]. The equilibrium heat capacity terms as formulated in SAND2019-12917CTF [8] exhibited undesirable behaviors that were identified in SAND2021-11193 [1]. Accordingly, the equilibrium heat

capacity terms were modified to eliminate the undesirable behavior in SAND2021-9851CTF [9]. However, by studying the form of the potential energy in Appendix B, it became clear that a certain symmetry must exist between the equilibrium and integral terms. To enforce that symmetry, the equilibrium heat capacity terms have been modified once again. Their current form is shown in Eq. (2.7). The new thermal terms have been verified as shown in Section 5.5.

Updated material clock for consistency with the PEC theory, and a flexible clock definition for backwards compatibility with older versions of Spectacular. The PEC model used four relaxation functions, one for each memory term in the free energy. The functions f_1 , f_2 , f_3 , and f_4 were related to volume, shear, thermal strain, and thermal relaxations, respectively. As part of simplifying PEC to SPEC, only f_1 and f_2 were kept, as it was assumed that $f_1 \approx f_3 \approx f_4$. Following the previous PEC theory, Spectacular uses four independent relaxation functions. To be consistent with the PEC theory, f_4 should appear in the thermal memory term of the clock and f_3 should appear in the volume memory term of the clock. However, because previous versions of Spectacular did not include thermal terms, older versions of Spectacular used f_3 and f_1 in the thermal and volume memory terms, respectively. For backwards compatibility with calibrations generated using the older Spectacular code, users can choose the relaxation functions used with the thermal and volume terms in the clock. The user's choices for the relaxation functions in the thermal and volume terms are represented by the indices T and V, respectively, in Eq. (2.46).

New parameter for deactivating thermal history in the clock. A new parameter C_0 was added that allows the user to deactivate the thermal memory term in the clock. The only choice consistent with the PEC and SPEC theories is $C_0 = 1$, but setting $C_0 = 0$ may be useful for reducing coupling when formulating verification exercises. Furthermore, when $C_0 = C_3 = C_4 = 0$, all memory terms in the clock are deactivated and the clock reduces to an explicit function of temperature. The new parameter C_0 appears in Eq. (2.46).

Improved robustness by allowing the Newton–Raphson method to restart from the equilibrium solution. Typically, the Newton–Raphson method in Spectacular uses the converged shift factor from the previous timestep as the initial guess for the current timestep. However, when the model is heated from a state with a high shift factor, the memory terms may suddenly relax to zero over a single timestep. When this happens, the previously converged shift factor is a poor initial guess and prevents the Newton–Raphson method from converging. Often, when this happens, using the equilibrium shift factor as the initial guess allows the Newton–Raphson method to converge. To improve the robustness of the model, if the Newton–Raphson method fails, it is restarted using the equilibrium shift factor as the initial guess. A more complete description of the equilibrium restart is given in Section 4.2.2.

Addition of state variables for qualitatively comparing the PEC and SPEC material clocks.

State variables were added to the model that enable comparisons between the PEC and SPEC material clocks. However, because of the implicit nature of the clocks, the PEC clock variables are only useful for qualitative comparisons between the two model forms. For thermo-mechanical

histories where the PEC and SPEC clocks give approximately equal values for the shift factor, the two model forms should predict approximately the same constitutive behavior. However, when the two clocks are different, it is only possible to know that PEC would predict a different constitutive response than SPEC, but it is not possible to quantitatively determine the response without actually running the PEC model. This is because the PEC clock is only included as a state variable, and so its memory terms are relaxing according to the SPEC clock shift factor. The theory for converting the PEC clock to the SPEC clock is shown in Appendix B, and the syntax for outputting the PEC clock state variables is shown in Chapter 6.

1. INTRODUCTION

The motivation for this reoprt is described in Section 1.1 and an overview of the contents is given in Section 1.2. The mathematical conventions used in this report are defined in Section 1.3.

1.1. Motivation

At Sandia National Laboratories, many epoxies and other glass-formers are modeled using the Simplified Potential Energy Clock (SPEC) constitutive model [7], which has been implemented in LAMÉ [10] as the UNIVERSAL_POLYMER model. Throughout the years, the SPEC model form has been augmented in a development code known as Spectacular (stylized as SPECTACULAR when specifically referring to the LAMÉ implementation). Prior to this report, almost no formal documentation existed for Spectacular. Instead, new developers had to learn about Spectacular by reading the documentation for UNIVERSAL_POLYMER, then discovering how the two models differ through discussions with subject matter experts and direct examination of the SPECTACULAR code. As the differences between SPEC and Spectacular increase, this approach is becoming less sustainable, as it creates unnecessary barriers for analysts to use the model and for developers to improve the model. Therefore, the goal of this report is to provide a comprehensive theory document for the Spectacular constitutive model, thereby preserving knowledge currently held by only a few Sandia viscoelasticians.

1.2. Overview of material in this report

In Chapter 2, the Spectacular model theory is described in sufficient detail to understand the model in the context of quasi-static mechanical calculations with a prescribed temperature field, as one might do in Sierra/SM [11] (also known as Adagio). For engineers and researchers that are first learning about SPEC or Spectacular, this is a good starting point.¹ More advanced material is presented in Chapters 3 and 4. In Chapter 3, a complete set of constitutive equations for thermo-mechanical calculations is derived. The derivation starts with the expression for the Helmholtz free energy, then expressions for the stress and entropy are derived according to the rational mechanics framework [13]. Chapter 3 also discusses the theory necessary for using Spectacular in coupled thermo-mechanical simulations with Adagio and Aria. In Chapter 4, the numerical methods for time-integrating the model are shown, which includes methods for updating the hereditary integrals and a description of the Newton-Raphson method used to solve for the shift factor. In Chapter 5, SPECTACULAR is verified under limited conditions. Chapter 5 also demonstrates new model features, and shows how they address previously identified model form errors. Chapter 6 is a user guide for deploying SPECTACULAR in Sierra/SM calculations. It describes the syntax used to define the model parameters and describes the state variables available for output. Future work and prospects for the model are described in Chapter 7.

¹However, for those unfamiliar with the integral form of viscoelasticity, Chapter I in Christensen's book *Theory of Viscoelasticity* [12] provides a more didactic introduction to viscoelasticity in general. Also, Chapters III and VIII in that same text introduce thermo-viscoelasticity and nonlinear viscoelasticity, both of which are useful for understanding the Spectacular theory.

This report also contains a handful of appendices covering minor details of the model theory. In Appendix A, the temperature dependence of the cofficients of thermal expansion is described in more detail, which requires making the distinction between the *tangent* coefficients of thermal expansion (CTE) and the secant coefficients of thermal expansion. The distinction is important because the user inputs the tangent CTEs, but the model form is described using the secant CTEs. Appendix B describes the procedure used to simplify the potential energy used in the original PEC model clock to the state variable N, which is used in the current SPEC and Spectacular clocks. While this simplification procedure was thoroughly described in the first SPEC paper [7], the obtuse notation of the PEC model makes it difficult to follow without considerable effort. The authors hope that the discussion in Appendix B is more easily followed for a casual reading of the text. Appendix C shows how to apply the Leibniz integral rule to take derivatives of the hereditary integrals in Spectacular. The Leibniz integral rule may also be referred to as differentiation under the integral sign. Although the Leibniz rule is not conceptually difficult, it is not always taught in modern undergraduate calculus courses. By placing the rule in a self-contained appendix, the first author hopes to point future researchers to more formal citations for the rule than, say, a Wikipedia article. Finally, Appendices D and E show model parameters used for simulations in Chapter 5.

1.3. Mathematical conventions

In this report, direct notation for tensors is favored over indicial notation (i.e., summation conventions for repeated indices). This is because the tensor math in Spectacular is straightforward, and indices are useful for representing the relaxation functions and their Prony series, which do not follow the summation convention. First and second rank Cartesian tensors are represented using bold symbols. For clarity, common tensor operations are defined once here in terms of indicial notation:

$$\left(\boldsymbol{A}^{\mathsf{T}}\right)_{ij} = A_{ji}, \qquad \operatorname{tr} \boldsymbol{A} = A_{ii}, \qquad \left(\boldsymbol{A} \cdot \boldsymbol{B}\right)_{ij} = A_{im}B_{mj}, \qquad \boldsymbol{A} : \boldsymbol{B} = A_{mn}B_{mn}.$$
(1.1)

An overdot signifies the total time derivative while keeping the material point fixed;

$$\dot{A} = \frac{\mathrm{d}A}{\mathrm{d}t}\Big|_{\boldsymbol{X}},\tag{1.2}$$

where **X** is the position vector to the material point in the reference configuration. Spatial derivatives with respect to the *reference* configuration are written using ∇ . For example,

$$\nabla \boldsymbol{\theta} = \frac{\partial \boldsymbol{\theta}}{\partial X_i} \hat{\boldsymbol{e}}_i, \qquad \nabla \cdot \boldsymbol{Q} = \frac{\partial Q_i}{\partial X_i}, \qquad (1.3)$$

where $\hat{\boldsymbol{e}}_i$ is the Cartesian unit vector for component X_i of the reference configuration position vector \boldsymbol{X} . Spatial derivatives with respect to the *current* configuration are written using text. For example,

grad
$$\theta = \frac{\partial \theta}{\partial x_i} \hat{\boldsymbol{e}}_i,$$
 div $\boldsymbol{q} = \frac{\partial q_i}{\partial x_i},$ (1.4)

where $\hat{\boldsymbol{e}}_i$ is the Cartesian unit vector for component x_i of the current configuration position vector \boldsymbol{x} . The decadic logarithm (base 10) is denoted using log and the natural logarithm is denoted using ln.

2. MODEL THEORY

In this chapter, the model theory is presented at a level of detail that is sufficient to (1) describe the mechanical behavior represented by the model, and (2) connect all model inputs to the model theory. A more complete description of the thermo-mechanical behavior is shown in Chapter 3.

2.1. Model summary

Spectacular is an isotropic, nonlinear viscoelastic constitutive model for amorphous polymers and other glass-forming materials. It comes from a family of potential energy clock models, the first of which was the Potential Energy Clock model, or PEC [5, 6]. The most recent published variant of the PEC model is the Simplified Potential Energy Clock model, or SPEC [7]. Spectacular is an extension of SPEC that has gradually evolved over several years as small improvements are incorporated. The Spectacular model is built from a Helmholtz free energy that is a functional depending on the histories of strain and temperature. Thermodynamically-consistent stress and entropy functionals are then derived from the free energy using a Coleman-Noll procedure [13, 7]. The relaxation processes in the model are based on the material time-scale t^* , which is related to the laboratory timescale t through a highly nonlinear shift factor a. This shift factor, sometimes referred to as the material clock, is also a functional that depends on the histories of strain and temperature. In the original PEC model, the shift factor was a function of the potential energy, but only essential terms in the shift factor were kept in SPEC, so the shift factor in SPEC literally depends on a simplified potential energy. The use of the simplified potential energy for the shift factor is maintained in Spectacular.

2.2. Kinematics

Spectacular uses the integrated unrotated rate of deformation tensor $\boldsymbol{\varepsilon}$ as the strain measure,

$$\boldsymbol{\varepsilon} = \int_0^t \boldsymbol{d} \, \mathrm{d}s, \qquad \boldsymbol{D} = \boldsymbol{R} \cdot \boldsymbol{d} \cdot \boldsymbol{R}^\mathsf{T}, \qquad \boldsymbol{D} = \frac{1}{2} \left(\boldsymbol{L} + \boldsymbol{L}^\mathsf{T} \right), \qquad \boldsymbol{F} = \boldsymbol{R} \cdot \boldsymbol{U}, \qquad (2.1)$$

where *d* is the unrotated rate of deformation tensor, *D* is the rate of deformation tensor, *L* is the velocity gradient, and *R* and *U* are the rotational and right stretch parts of the deformation gradient, *F*. Although integrating *d* does not actually produce a strain measure, the integrated unrotated rate of deformation tensor ε is a good approximation for the Hencky strain *H* [7], i.e. $\varepsilon \approx H$ in certain cases. The Spectacular model uses the following strain invariants

$$I_1 = \operatorname{tr} \boldsymbol{\epsilon}, \qquad I_2 = \operatorname{tr} (\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}), \qquad I_3 = \operatorname{tr} (\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}). \qquad (2.2)$$

The deviatoric part of the strain *e* is written as

$$\boldsymbol{e} = \boldsymbol{\varepsilon} - \frac{I_1}{3} \boldsymbol{1}, \tag{2.3}$$

where 1 is the second-order identity tensor.

2.3. Helmholtz free energy

Spectacular postulates a general time-dependent Hemlholtz free energy functional that depends on the previous histories of strain and temperature,

$$\Psi(t) = \mathfrak{P}_{s=-\infty}^{s=t} \Big\{ \mathbf{\epsilon}(s), \mathbf{\theta}(s), a(s); \mathbf{\epsilon}, \mathbf{\theta} \Big\},$$
(2.4)

where $\Psi(t)$ is the Helmholtz free energy at the current time t, $\mathbf{\varepsilon}(s)$, $\theta(s)$, and a(s) are the histories of the strain, temperature, and the shift factor as functions of time, and \mathfrak{P} represents the Helmholtz free energy functional. The free energy functional also depends on the current values of temperature and strain, $\mathbf{\varepsilon} = \mathbf{\varepsilon}(t)$, $\theta = \theta(t)$.² The functional notation in Eq. (2.4) implies that the history of the material extending infinitely backwards in time is required as input. Clearly, such a requirement is impractical. Instead, some initial time t = 0 is chosen where the material is in an equilibrium state and therefore past history is irrelevant. In practice, this is almost always accomplished by choosing t = 0 at some temperature above the material's glass transition temperature. When history before t = 0 is neglected, the general form of the functional becomes

$$\Psi(t) = \mathfrak{P}_{s=0}^{s=t} \Big\{ \mathbf{\varepsilon}(s), \theta(s), a(s); \mathbf{\varepsilon}, \theta \Big\}.$$
(2.5)

This general form can be made specific through a Fréchet expansion [14, 15, 13, 16, 4], which is essentially a Taylor series for functionals [5]. The Helmholtz free energy form used by Spectacular is obtained by expanding Eq. (2.5) through second order terms [14, 16],

$$\Psi(t) = \Psi_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}) + \frac{1}{2} K_D(\mathbf{\epsilon}, \mathbf{\theta}) \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du + G_D(\mathbf{\epsilon}, \mathbf{\theta}) \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \frac{d\mathbf{e}}{ds} : \frac{d\mathbf{e}}{du} \, ds \, du - L_D(\mathbf{\epsilon}, \mathbf{\theta}) \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\mathbf{\theta}}{du} \, ds \, du - \frac{C_D(\mathbf{\theta})}{2\mathbf{\theta}_{ref}} \int_0^t \int_0^t f_4(t^* - s^*, t^* - u^*) \frac{d\mathbf{\theta}}{ds} \frac{d\mathbf{\theta}}{du} \, ds \, du.$$
(2.6)

The "D" subscript denotes a difference between the glassy and rubbery values of a property, with K and G for the bulk and shear moduli, L for the thermal pressure, and C for the contsant volume

²This notation is not fully rigorous, but has been carefully chosen to capture the main ideas that are of interest to a constitutive modeler. First of all, it is somewhat redundant to include the current values of $\boldsymbol{\varepsilon}(t)$ and $\theta(t)$ along with their histories. However, this notational choice was made to emphasize that the Helmholtz free energy has essentially two parts: equilibrium terms that depend on the current values of the state variables $\{\boldsymbol{\varepsilon}(t), \theta(t)\}$ and non-equilibrium terms that depend on the histories of the state variables $\{\boldsymbol{\varepsilon}(s), \theta(s), a(s)\}_{s=-\infty}^{s=t}$. Second, the dependence of the free energy functional on a(s) is implicit; a(s) does not appear in the equation for $\Psi(t)$, but is needed to transform the material time coordinate t^* (where the thermodynamics are naturally formulated) to the laboratory time coordinate t (where the constitutive model must be time-integrated). Despite the implicit dependence of the free energy functional on a(s), it is included as an argument because the residual functions for the time-integration scheme are explicit functions of a at the previous and current timesteps (a_n and a_{n+1}).

heat capacity (these will be described in more detail in 2.4). The equilibrium contribution to the free energy, $\Psi_{\infty}(\boldsymbol{\epsilon}, \boldsymbol{\theta})$, depends only on the current strain and temperature. Its expression is

$$\Psi_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) = \frac{1}{2} K_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) I_{1}^{2} + G_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) \boldsymbol{e} : \boldsymbol{e} - L_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) (\boldsymbol{\theta} - \boldsymbol{\theta}_{sf}) I_{1} - \frac{C_{\infty}(\boldsymbol{\theta})}{2\boldsymbol{\theta}_{ref}} (\boldsymbol{\theta} - \boldsymbol{\theta}_{ref})^{2}.$$
(2.7)

The " ∞ " subscript denotes the equilibrium, (i.e., rubbery) value of property. Two fixed temperatures appear in Eqs. (2.6) and (2.7). The first is the reference temperature θ_{ref} , which is the temperature where the shift factor is one under traction-free, equilibrium conditions (the shift factor will be defined in Section 2.6). The second is the stress-free temperature θ_{sf} , which is the temperature where the thermal strain is defined to be zero under equilibrium and free-expansion (i.e., traction free) conditions. The stress-free temperature can be chosen, so long as $\theta_{sf} \ge \theta_{ref}$. Typically, the model should be initialized at the stress-free temperature; $\theta(0) = \theta_{sf}$.

The non-equilibrium (or memory) contributions to the free energy arise from the four convolution integrals in Eq. (2.6), each of which has its own kernel denoted as $f_r(x,y)$, with $r \in \{1, 2, 3, 4\}$. These kernels are referred to as relaxation functions and are respectively called the volumetric or bulk relaxation function (f_1) , the shear relaxation function (f_2) , the thermal-volumetric or thermal strain relaxation function (f_3) , and the thermal relaxation function (f_4) . To maintain coherence with physical observations, the relaxation functions must obey four constraints: (1) they must be symmetric with respect to their arguments, (2) they must equal one in the unrelaxed state, (3) they must limit to zero in the relaxed state, and (4) they must decrease monotonically from one to zero. In mathematical terms,

$$f_r(x,y) = f_r(y,x),$$
 (2.8)

$$f_r(0,0) = 1, (2.9)$$

$$\lim_{x \to \infty} f_r(x, y) = \lim_{y \to \infty} f_r(x, y) = 0,$$
(2.10)

$$\frac{\partial f_r}{\partial x} \le 0. \tag{2.11}$$

Because the arguments of the relaxation functions are symmetric, it is often convenient to use a shorthand where a zero argument is suppressed;

$$f_r(x) \coloneqq f_r(x,0) = f_r(0,x).$$
 (2.12)

The time arguments for the relaxation functions in Eq. (2.6) are marked with a superscript "*". This indicates that relaxation occurs on the material time scale, which is shifted from the laboratory timescale by the material clock. The shifted time will be defined later with the discussion of the material clock in Section 2.6.

The remaining terms in Eqs. (2.6) and (2.7) will be described in Section 2.4.

2.4. Equilibrium and instantaneous viscoelastic limits

Four types of functions related to the instantaneous (i.e., glassy) and equilibrium (i.e., rubbery) limiting responses appear in Eqs. (2.6) and (2.7). These four functions are related to the bulk

modulus *K*, the shear modulus *G*, the (secant) volumetric coefficient of thermal expansion (CTE) δ , and the constant volume heat capacity (per reference volume) *C*. The instantaneous and equilibrium limits are marked with subscripts "g" and " ∞ ", respectively. All of these functions are allowed up to a linear dependence on temperature and they depend on the strain through a linear relationship with the three strain invariants defined in Eq. (2.2). The instantaneous limits are defined as

$$K_{g}(\mathbf{\epsilon}, \mathbf{\theta}) = K_{g}^{\text{ref}} + K_{g}^{\mathbf{\theta}}(\mathbf{\theta} - \mathbf{\theta}_{\text{ref}}) + K_{g}^{I_{1}}I_{1} + K_{g}^{I_{2}}I_{2} + K_{g}^{I_{3}}I_{3}, \qquad (2.13)$$

$$G_g(\mathbf{\epsilon}, \mathbf{\theta}) = G_g^{\text{ref}} + G_g^{\mathbf{\theta}}(\mathbf{\theta} - \mathbf{\theta}_{\text{ref}}) + G_g^{I_1} I_1 + G_g^{I_2} I_2 + G_g^{I_3} I_3, \qquad (2.14)$$

$$\delta_g(\theta) = \delta_g^{\text{ref}} + \delta_g^{\theta}(\theta - \theta_{\text{ref}}), \qquad (2.15)$$

$$C_g(\theta) = C_g^{\text{ref}} + C_g^{\theta}(\theta - \theta_{\text{ref}}), \qquad (2.16)$$

where each coefficient is a model input and constant terms with a superscript "ref" indicate the value of that limiting response at temperature θ_{ref} and zero strain. The same forms are used for the equilibrium limits;

$$K_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}) = K_{\infty}^{\text{ref}} + K_{\infty}^{\mathbf{\theta}}(\mathbf{\theta} - \mathbf{\theta}_{\text{ref}}) + K_{\infty}^{I_1} I_1 + K_{\infty}^{I_2} I_2 + K_{\infty}^{I_3} I_3, \qquad (2.17)$$

$$G_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}) = G_{\infty}^{\text{ref}} + G_{\infty}^{\mathbf{\theta}}(\mathbf{\theta} - \mathbf{\theta}_{\text{ref}}) + G_{\infty}^{I_1} I_1 + G_{\infty}^{I_2} I_2 + G_{\infty}^{I_3} I_3, \qquad (2.18)$$

$$\delta_{\infty}(\theta) = \delta_{\infty}^{\text{ref}} + \delta_{\infty}^{\theta} \left(\theta - \theta_{\text{ref}}\right), \qquad (2.19)$$

$$C_{\infty}(\theta) = C_{\infty}^{\text{ref}} + C_{\infty}^{\theta}(\theta - \theta_{\text{ref}}).$$
(2.20)

The CTE functions enter into Eqs. (2.6) and (2.7) as products with the bulk moduli functions, called the thermal pressure,

$$L_g(\mathbf{\epsilon}, \mathbf{\theta}) = K_g(\mathbf{\epsilon}, \mathbf{\theta}) \,\delta_g(\mathbf{\theta}), \qquad \qquad L_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}) = K_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}) \,\delta_{\infty}(\mathbf{\theta}). \tag{2.21}$$

Predictably, the equilibrium responses appear in the expression for the equilibrium free energy, Eq. (2.7). The difference between the instantaneous and equilibrium limit for each function is denoted with a subscript "D",

$$K_D(\mathbf{\epsilon}, \mathbf{\theta}) = K_g(\mathbf{\epsilon}, \mathbf{\theta}) - K_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}), \qquad G_D(\mathbf{\epsilon}, \mathbf{\theta}) = G_g(\mathbf{\epsilon}, \mathbf{\theta}) - G_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}), \qquad (2.22)$$

$$L_D(\mathbf{\epsilon}, \mathbf{\theta}) = L_g(\mathbf{\epsilon}, \mathbf{\theta}) - L_{\infty}(\mathbf{\epsilon}, \mathbf{\theta}), \qquad C_D(\mathbf{\theta}) = C_g(\mathbf{\theta}) - C_{\infty}(\mathbf{\theta}). \qquad (2.23)$$

These differences appear as coefficients to the hereditary integrals in Eq. (2.6).

Derivatives of these viscoelastic limits with respect to strain will appear later in the equation for the stress. The derivatives of the equilibrium functions with respect to strain are

$$\frac{\partial K_{\infty}}{\partial \boldsymbol{\varepsilon}} = K_{\infty}^{I_1} \mathbf{1} + 2K_{\infty}^{I_2} \boldsymbol{\varepsilon} + 3K_{\infty}^{I_3} \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}, \qquad (2.24)$$

$$\frac{\partial G_{\infty}}{\partial \boldsymbol{\varepsilon}} = G_{\infty}^{I_1} \mathbf{1} + 2G_{\infty}^{I_2} \boldsymbol{\varepsilon} + 3G_{\infty}^{I_3} \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}, \qquad (2.25)$$

$$\frac{\partial L_{\infty}}{\partial \boldsymbol{\varepsilon}} = \left(K_{\infty}^{I_1} \mathbf{1} + 2K_{\infty}^{I_2} \boldsymbol{\varepsilon} + 3K_{\infty}^{I_3} \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon} \right) \delta_{\infty}(\boldsymbol{\theta}), \qquad (2.26)$$

$$\frac{\partial C_{\infty}}{\partial \mathbf{\epsilon}} = 0. \tag{2.27}$$

Derivatives of the instantaneous limits follow the same form. Derivatives of the viscoelastic limits with respect to temperature will appear in the entropy equation and equations for

thermo-mechanical coupling, presented in Chapter 3. The derivatives of the equilibrium functions with respect to temperature are

$$\frac{\partial K_{\infty}}{\partial \theta} = K_{\infty}^{\theta}, \qquad \qquad \frac{\partial G_{\infty}}{\partial \theta} = G_{\infty}^{\theta}, \qquad \qquad \frac{\partial C_{\infty}}{\partial \theta} = C_{\infty}^{\theta}, \qquad (2.28)$$

$$\frac{\partial L_{\infty}}{\partial \theta} = K_{\infty}^{\theta} \delta_{\infty} \left(\theta \right) + K_{\infty} \left(\boldsymbol{\varepsilon}, \theta \right) \delta_{\infty}^{\theta}, \qquad (2.29)$$

$$\frac{\partial^2 L_{\infty}}{\partial \boldsymbol{\varepsilon} \partial \boldsymbol{\theta}} = \left(K_{\infty}^{I_1} \mathbf{1} + 2K_{\infty}^{I_2} \boldsymbol{\varepsilon} + 3K_{\infty}^{I_3} \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon} \right) \delta_{\infty}^{\boldsymbol{\theta}}, \tag{2.30}$$

$$\frac{\partial^2 L_{\infty}}{\partial \theta^2} = 2K_{\infty}^{\theta} \delta_{\infty}^{\theta}.$$
(2.31)

Derivatives of the instantaneous functions follow the same form.

- -

The Spectacular model equations use the secant CTE δ , but the tangent CTE α is more commonly measured in experiments. To clarify, the secant and tangent CTE are defined under free expansion conditions as

$$\delta(\theta) \coloneqq \frac{I_1}{\theta - \theta_{\rm sf}}, \qquad \qquad \alpha(\theta) \coloneqq \frac{\mathrm{d}I_1}{\mathrm{d}\theta}. \tag{2.32}$$

The model inputs used to define the thermal expansion behavior actually define the tangent CTE, which is also allowed to depend linearly on temperature;

$$\alpha_g(\theta) = \alpha_g^{\text{ref}} + \alpha_g^{\theta}(\theta - \theta_{\text{ref}}), \qquad \alpha_{\infty}(\theta) = \alpha_{\infty}^{\text{ref}} + \alpha_{\infty}^{\theta}(\theta - \theta_{\text{ref}}). \qquad (2.33)$$

Internally, the model converts the tangent CTE to a secant CTE using the following:

$$\delta_{g}^{\text{ref}} = \alpha_{g}^{\text{ref}} + \frac{1}{2} \alpha_{g}^{\theta} (\theta_{\text{sf}} - \theta_{\text{ref}}), \qquad \delta_{\infty}^{\text{ref}} = \alpha_{\infty}^{\text{ref}} + \frac{1}{2} \alpha_{\infty}^{\theta} (\theta_{\text{sf}} - \theta_{\text{ref}}), \qquad (2.34)$$

$$\delta_g^{\theta} = \frac{1}{2} \alpha_g^{\theta}, \qquad \qquad \delta_{\infty}^{\theta} = \frac{1}{2} \alpha_{\infty}^{\theta}. \qquad (2.35)$$

The derivation for Eqs. (2.34) and (2.35) is shown in Appendix A.

2.5. Stress

Using a standard Colemann-Noll procedure [13, 7], the stress tensor Σ , which is the stress measure that is work-conjugate to d, is derived in terms of the Helmholtz free energy as

$$\Sigma(t) = \frac{\partial \Psi}{\partial \varepsilon}.$$
(2.36)

For implementation into a finite element code, Σ is either converted to the unrotated Cauchy stress T or the Cauchy stress σ , depending on the specific finite element code. To convert between the different stress tensors, one can use

$$\boldsymbol{T} = \frac{\boldsymbol{\rho}}{\boldsymbol{\rho}_0} \boldsymbol{\Sigma} = \frac{\boldsymbol{\Sigma}}{\det \boldsymbol{F}}, \qquad \boldsymbol{\sigma} = \boldsymbol{R} \cdot \boldsymbol{T} \cdot \boldsymbol{R}^{\mathsf{T}}. \qquad (2.37)$$

The stress Σ can also be thought of as a functional, expressed as

$$\Sigma(t) = \underset{s=0}{\overset{s=t}{\mathfrak{S}}} \left\{ \varepsilon(s), \theta(s), a(s); \varepsilon, \theta \right\}, \qquad (2.38)$$

$$\Sigma(t) = \Sigma_{\infty}(\varepsilon, \theta) + K_D(\varepsilon, \theta) \mathbf{1} \int_0^t f_1(t^* - s^*) \frac{dI_1}{ds} ds$$

$$+ 2G_D(\varepsilon, \theta) \int_0^t f_2(t^* - s^*) \frac{de}{ds} ds$$

$$-L_D(\varepsilon, \theta) \mathbf{1} \int_0^t f_3(t^* - s^*) \frac{d\theta}{ds} ds$$

$$+ \frac{1}{2} \frac{\partial K_D}{\partial \varepsilon} \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du$$

$$+ \frac{\partial G_D}{\partial \varepsilon} \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \frac{de}{ds} : \frac{de}{du} ds du$$

$$- \frac{\partial L_D}{\partial \varepsilon} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du,$$

with the equilibrium contribution to the stress Σ_{∞} being

$$\boldsymbol{\Sigma}_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) = K_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})I_{1}\boldsymbol{1} + 2G_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})\boldsymbol{e} - L_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})(\boldsymbol{\theta} - \boldsymbol{\theta}_{\mathrm{sf}})\boldsymbol{1} + \frac{1}{2}\frac{\partial K_{\infty}}{\partial \boldsymbol{\varepsilon}}I_{1}^{2} + \frac{\partial G_{\infty}}{\partial \boldsymbol{\varepsilon}}\boldsymbol{e}:\boldsymbol{e} - \frac{\partial L_{\infty}}{\partial \boldsymbol{\varepsilon}}I_{1}(\boldsymbol{\theta} - \boldsymbol{\theta}_{\mathrm{sf}}).$$
(2.40)

When the viscoelastic limits are taken as constants, Eqs. (2.39) and (2.40) simplify to a form that is more common in viscoelasticity and more intuitive:

$$\boldsymbol{\Sigma}(t) = \left\{ K_{\infty} \left(I_1 - \delta_{\infty} \left(\theta - \theta_{\rm sf} \right) \right) + K_D \int_0^t f_1 \left(t^* - s^* \right) \frac{\mathrm{d}I_1}{\mathrm{d}s} \,\mathrm{d}s - L_D \int_0^t f_3 \left(t^* - s^* \right) \frac{\mathrm{d}\theta}{\mathrm{d}s} \,\mathrm{d}s \right\} \mathbf{1} + 2G_{\infty} \boldsymbol{e} + 2G_D \int_0^t f_2 \left(t^* - s^* \right) \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s} \,\mathrm{d}s.$$
(2.41)

2.6. Clock definition

The shift factor *a* relates the laboratory timescale d*t* to the material timescale d*t*^{*}. A difference in material time $t^* - s^*$ is related to a difference in the laboratory time t - s by

$$a dt^* = dt,$$
 $t^* - s^* = \int_s^t \frac{du}{a(u)}.$ (2.42)



Figure 2-1 The WLF equation, the Arrhenius equation, and the piecewise shift factor function used by Spectacular, Eq. (2.43). $C_1 = 10$, $C_2 = 50$ K, $\theta_{ref} = 100$ °C, $N_{match} = 85$ °C, $A_2 = 20000$ K. A_1 is calculated according to Eq. (2.44) to ensure the two pieces of the function join at N_{match} .

The shift factor *a* is defined through a piecewise function that depends on the state variable N(t), which has units of temperature. The shift factor function has a Williams-Landel-Ferry (WLF) form [17] for $N \ge N_{\text{match}}$ and an Arrhenius form [18] for $N < N_{\text{match}}$,

$$\log a(N(t)) = \begin{cases} -\frac{C_{1}(N - \theta_{\text{ref}})}{C_{2} + N - \theta_{\text{ref}}}, & N \ge N_{\text{match}}, \\ \\ A_{1} + \frac{A_{2}}{N}, & N < N_{\text{match}}. \end{cases}$$
(2.43)

The shift factor function $\log a(N)$ is fully defined from the parameters θ_{ref} , C_1 , C_2 , A_2 , and N_{match} . The parameter A_1 is not independent to ensure continuity between the two pieces at N_{match} ,

$$A_1 = -\frac{A_2}{N_{\text{match}}} - \frac{C_1 \left(N_{\text{match}} - \theta_{\text{ref}} \right)}{C_2 + N_{\text{match}} - \theta_{\text{ref}}}.$$
(2.44)

Though continuous at N_{match} , the shift factor function is not smooth at N_{match} . The shift factor as a function of N (Eq. (2.43)) is plotted in Fig. 2-1.

In the original PEC model, the shift factor *a* was driven by the potential energy [5, 6]. The SPEC model used a simplified potential energy [7] that only kept essential terms, see Appendix B for details of the simplification procedure. To accommodate the severe reduction in terms, the coefficients to these essential terms were made into free parameters in Spectacular, where previously in SPEC they depended on the viscoelastic limits. The expression for the simplified

potential energy N is then

$$N(t) = \mathfrak{N}_{s=0}^{s=t} \Big\{ \mathbf{\varepsilon}(s), \mathbf{\theta}(s), a(s); \mathbf{\varepsilon}, \mathbf{\theta} \Big\},$$
(2.45)

$$N(t) = \theta - C_0 \int_0^t f_T (t^* - s^*) \frac{d\theta}{ds} ds + C_3 \left(I_1 - I_{1,ref} - \int_0^t f_V (t^* - s^*) \frac{dI_1}{ds} ds \right) + C_4 \int_0^t \int_0^t f_2 (t^* - s^*, t^* - u^*) \frac{d\mathbf{e}}{ds} : \frac{d\mathbf{e}}{du} ds du, V \in \{1, 3\}, T \in \{3, 4\},$$
(2.46)

where C_0 , C_3 , C_4 are clock parameters, and V and T are indices chosen by the user. The effect of volume strain on the shift factor is adjusted with C_3 , where a compressive volume strain will slow relaxation processes. This parameter allows the glass transition to change with pressure. The effect of shear strain on this shift factor is controlled through C_4 , where any shear strain speeds-up relaxation processes. This parameter allows for yield under both tension and compression. In SPEC, the thermal hereditary integral had a coefficient of one, $C_0 = 1$. In Spectacular, this coefficient is made into the parameter C_0 to enable developers to deactivate the influence of the temperature history on the shift factor. While this is useful for verification exercises and debugging, $C_0 = 1$ should always be used when modeling real materials. The indices V and T allow the user to determine which relaxation functions appear in the volume and thermal convolution integrals respectively. These choices are allowed for backwards compatibility with older versions of Spectacular, but V = 3 and T = 4 are the choices consistent with the original terms carried forward from PEC. In order to keep the equilibrium shift factor equal to one at θ_{ref} , the volume strain in Eq. (2.46) is offset by the volume strain that would occur under free expansion after cooling from θ_{sf} to θ_{ref} ,

$$I_{1,\text{ref}} = \delta_{\infty}^{\text{ref}} \left(\theta_{\text{ref}} - \theta_{\text{sf}} \right).$$
(2.47)

Although *N* may be referred to as the "simplified potential energy", *N* has units of temperature, so it may be more intuitive to refer to it as the "clock temperature". In SPEC, *N* included a $\theta - \theta_{ref}$ term, but the θ_{ref} term was removed to make *N* more like an absolute temperature. It is worth noting that *N* is also a functional that depends on the histories of strain, temperature, and the shift factor. Because *N* depends on the shift factor and the shift factor depends on *N*, Eq. (2.46) is an implicit equation. The primary challenge of numerically integrating the Spectacular model is simultaneously solving Eqs. (2.43) and (2.46).

The parameters C_1 , C_2 , N_{match} , and A_2 in Eq. (2.43) are not typically determined experimentally. Instead, it is more common in the literature to report the equilibrium shift factor as a function of temperature. Therefore, the model accepts parameters that define the equilibrium shift factor under free expansion as a function of temperature and then converts those parameters into the those used in Eq. (2.43). Assuming the equilibrium shift factor as a function of temperature follows a similar form to Eq. (2.43), then

$$\log \hat{a}_{\infty}(\theta) = \begin{cases} -\frac{\hat{C}_{1}(\theta - \theta_{\text{ref}})}{\hat{C}_{2} + \theta - \theta_{\text{ref}}}, & \theta \ge \theta_{\text{match}}, \\ \log \left[\hat{a}_{0} \exp \left(\frac{E_{a}}{R \theta} \right) \right], & \theta < \theta_{\text{match}}. \end{cases}$$
(2.48)

where \hat{C}_1 and \hat{C}_2 are the WLF coefficients [17], E_a is the activation energy, R is the gas constant, \hat{a}_0 is the shift factor at $E_a/(R\theta) = 1$, and θ_{match} is the temperature where the function switches from WLF to Arrhenius. The subscript ∞ on \hat{a}_{∞} is used to emphasize that this function is for the *equilibrium* shift factor, i.e., when all memory terms are zero. When defining the shift factor as a function of temperature, \hat{C}_1 , \hat{C}_2 , θ_{match} , and E_a/R are input instead of C_1 , C_2 , N_{match} , and A_2 . Like A_1 , the parameter \hat{a}_0 is dependent to ensure continuity at θ_{match} . Under equilibrium conditions, all memory integrals in Eq. (2.46) are zero. Under free expansion, $I_1 = \delta_{\infty}(\theta) (\theta - \theta_{sf})$. Therefore, the equilibrium clock temperature under free expansion depends only on the temperature,

$$N_{\infty}(\theta) = \theta + C_3 \left[\delta_{\infty}(\theta) \left(\theta - \theta_{\rm sf} \right) - I_{1,\rm ref} \right].$$
(2.49)

Thus, the equilibrium shift factor as a function of N can be written as

$$\log a_{\infty}(\theta) = \log a \left(N_{\infty}(\theta) \right) = \begin{cases} -\frac{C_1 \left(N_{\infty} - \theta_{\text{ref}} \right)}{C_2 + N_{\infty} - \theta_{\text{ref}}}, & N_{\infty} \ge N_{\text{match}}, \\ A_1 + \frac{A_2}{N_{\infty}}, & N_{\infty} < N_{\text{match}}. \end{cases}$$
(2.50)

The conversion from $\log \hat{a}_{\infty}(\theta)$ in Eq. (2.48) to $\log a(N_{\infty}(\theta))$ Eq. (2.50) is only approximate. When the temperature dependence of $\alpha_{\infty}(\theta)$ is neglected, the WLF parameters \hat{C}_1 and \hat{C}_2 are easily converted to C_1 and C_2 through algebraic manipulations of Eqs. (2.48) and (2.50):

$$C_1 = \hat{C}_1 \tag{2.51}$$

$$C_2 = \hat{C}_2 \left(1 + C_3 \alpha_{\infty}^{\text{ref}} \right).$$
(2.52)

When α_{∞}^{θ} is small (it usually is), the difference between the WLF parts of Eqs. (2.48) and (2.50) is insignificant. To convert θ_{match} to N_{match} , simply evaluate Eq. (2.49) at θ_{match} :

$$N_{\text{match}} = \theta_{\text{match}} + C_3 \left(\delta_{\infty} \left(\theta_{\text{match}} \right) \left(\theta_{\text{match}} - \theta_{\text{sf}} \right) - I_{1,\text{ref}} \right).$$
(2.53)

To convert E_a/R to A_2 , set the slopes of the Arrhenius parts of Eqs. (2.48) and (2.50) equal at θ_{match} ,

$$\frac{\partial \log \hat{a}}{\partial \theta}\Big|_{\theta^{-}_{\text{match}}} = \frac{\partial \log a}{\partial \theta}\Big|_{\theta^{-}_{\text{match}}},$$
(2.54)

which gives the following equation for calculating A_2 :

$$A_{2} = \frac{\left(\frac{E_{a}}{R\ln 10}\right) N_{\text{match}}^{2}}{\theta_{\text{match}}^{2} \left(1 + C_{3} \left[\delta_{\infty}^{\text{ref}} + \delta_{\infty}^{\theta} \left(2\theta_{\text{match}} - \theta_{\text{ref}} - \theta_{\text{sf}}\right)\right]\right)}.$$
(2.55)

This conversion is only exact when $C_3 = 0$, which is to say, it is almost never exact.

2.7. Specification of the relaxation functions

Requirements on the form of the relaxation functions were given in Eqs. (2.8) to (2.11), but the Spectacular model cannot practically accept any general function satisfying these requirements. To make the numerical integration of the hereditary integrals more tractable, a Prony series [19] is chosen as the form for the relaxation functions,

$$f_r(x,y) = \sum_{p=1}^{P_r} w_{rp} \exp\left(-\frac{x}{\tau_{rp}}\right) \exp\left(-\frac{y}{\tau_{rp}}\right),$$
(2.56)

where τ_{rp} and w_{rp} are the *p*-th Prony time and weight, respectively, in the relaxation function *r* with P_r number of Prony terms. In order to satisfy the requirements in Eqs. (2.9) and (2.11), the weights must all be positive and sum to one and the characteristic times must be positive;

$$\sum_{p=1}^{P_r} w_{rp} = 1, \qquad \qquad w_{rp} \ge 0, \qquad \qquad \tau_{rp} > 0.$$
 (2.57)

It is common to report the relaxation functions as stretched exponentials [20] instead of as a Prony series. A stretched exponential has the form

$$f_r(x,0) = f_r(x) = \exp\left[-\left(\frac{x}{\tau_r}\right)^{\beta_r}\right], \qquad \qquad 0 < \beta_r \le 1, \qquad (2.58)$$

where τ_r and β_r are the characteristic time and breadth for relaxation function *r*. Stretched exponential functions are also sometimes referred to as Kohlrausch-Williams-Watts (KWW) functions [21, 22, 20]. The model does not accept τ_r or β_r as inputs to define the relaxation functions, but it is convenient to discuss relaxation functions using stretched exponential fits because they use only two parameters instead of the $2P_r$ parameters associated with a Prony series. When this report discusses relaxation functions using stretched exponentials, it can be assumed that a Prony series was fit to the stretched exponential and that Prony series was input into the model to define the relaxation function.

3. THERMO-MECHANICAL COUPLING

3.1. Introduction

Spectacular is a full thermodynamic equation of state, and, as such, it is suitable for coupled thermo-mechanial calculations. A full thermo-mechanical theory is especially important for predicting physical aging, where deformation and viscoelastic relaxation may lead to small, but important, temperature changes. Furthermore, physical aging predictions are highly sensitive to the choice of f_4 , which can be determined by fitting the heat capacity predicted by the thermo-mechanical theory to measurements from differential scanning calorimetry (DSC).

This chapter describes the Spectacular theory for the case when, in addition to the deformation, the temperature is a degree of freedom. Two goals must be achieved to add temperature as a degree of freedom. First, a full set of thermodynamic constitutive equations must be developed to close the system of equations that define a thermodynamic process. Second, the energy balance equation must be cast in the form of a partial differential equation that can be numerically solved for the temperature field. The outline of this chapter is as follows. Preliminaries are addressed in Section 3.2, which gives a mathematical definition for a thermodynamic process and identifies the four constitutive equations necessary to close the system of equations describing a thermodynamic process. Section 3.3 describes the development of thermodynamically consistent constitutive equations for materials with memory that relax on a material timescale [13, 16]. In Section 3.3.1 the theory is developed in general terms, and then is applied to the Spectacular model in Section 3.4. Finally, Section 3.5 shows how to calculate the instantaneous heat capacity from Spectacular model state variables. This text of this chapter draws extensively from Refs. [13, 9].

For convenient referencing, certain fundamental equations are given special labels. The conservation of linear momentum is labelled as Eq. (P). The first and second laws of thermodynamics are labelled as Eqs. (I) and (II). The heat equation is labelled as Eq. (H).

3.2. Definition of a thermodynamic process

A thermodynamic process for a continuum body is described by eight functions of X and t, where X is the position vector for the material points in the reference configuration and t is the time. The eight functions that make up a thermodynamic process are as follows [13]

- 1. The position vector for the material points in the current configuration, $\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$. For a solid mechanics constitutive model it is often more convenient to track the deformation of material points using the strain, which is easily calculated for a given $\mathbf{x}(\mathbf{X}, t)$. Specifically, Spectacular uses the integrated unrotated rate of deformation tensor $\mathbf{\varepsilon} = \mathbf{\varepsilon}(\mathbf{X}, t)$, see Eq. (2.1).
- 2. The internal body forces, quantified by the stress tensor $\Sigma = \Sigma(X, t)$, where Σ is the stress conjugate to ε . Equally valid choices are the Cauchy stress tensor σ and the first

Piola-Kirchhoff stress tensor $\boldsymbol{P} = J\boldsymbol{\sigma} (\boldsymbol{F}^{-1})^{\mathsf{T}}$, where $J = \det \boldsymbol{F} = \rho_0 / \rho$. The Cauchy stress can be calculated from $\boldsymbol{\Sigma}$ using Eq. (2.37).

- 3. The body force $\boldsymbol{b} = \boldsymbol{b}(\boldsymbol{X}, t)$.
- 4. The entropy $\eta = \eta (\boldsymbol{X}, t)$.
- 5. The absolute temperature $\theta = \theta(\mathbf{X}, t)$.
- 6. The thermodynamic potential, commonly described using the internal energy $E = E(\mathbf{X}, t)$. For Spectacular, it will be more convenient to use the Helmholtz free energy $\Psi = \Psi(\mathbf{X}, t)$, where $\Psi = E - \theta \eta$. Another valid thermodynamic potential is the enthalpy $\chi = \chi(\mathbf{X}, t)$, where $\chi = E - \mathbf{P} : \mathbf{F}$.
- 7. The referential heat flux vector $\boldsymbol{Q} = \boldsymbol{Q}(\boldsymbol{X}, t)$, or alternatively, the spatial heat flux vector $\boldsymbol{q} = (1/J)\boldsymbol{F} \cdot \boldsymbol{Q}$.
- 8. The heat source $r = r(\mathbf{X}, t)$.

All intrinsic thermodynamic properties (η, E, Ψ) and distributed quantities (\boldsymbol{b}, r) are defined per unit volume in the reference configuration with volume V_0 and density ρ_0 . It is assumed that $\boldsymbol{b}(\boldsymbol{X},t)$ and $r(\boldsymbol{X},t)$ are known (in a finite element analysis, they are usually specified by the user). Therefore, six unknown field variables remain to be determined.

A thermodynamic process is restricted by the conservation of linear momentum and the first law of thermodynamics. The conservation of linear momentum in terms of the Piola-Kirchhoff stress tensor is

$$\nabla \cdot \boldsymbol{P} + \boldsymbol{b} = \rho_0 \boldsymbol{\ddot{x}},\tag{P}$$

where an overdot signifies the material time derivative (i.e., \boldsymbol{X} is fixed), and $\nabla \cdot ()$ signifies the divergence with respect to the reference configuration (i.e., $\nabla \cdot \boldsymbol{P} = (\partial P_{ij}/\partial X_j)\hat{\boldsymbol{e}}_i$). The first law of thermodynamics (conservation of energy) in the reference configuration is

$$\dot{E} - \boldsymbol{\Sigma} : \dot{\boldsymbol{\varepsilon}} + \nabla \cdot \boldsymbol{Q} - r = 0, \tag{I}$$

where, once again, $\nabla \cdot ()$ signifies the divergence with respect to the reference configuration (i.e., $\nabla \cdot \mathbf{Q} = \partial Q_i / \partial X_i$). In summary there are six unknown field variables ($\boldsymbol{\epsilon}, \boldsymbol{\Sigma}, \boldsymbol{\eta}, \boldsymbol{\Psi}, \boldsymbol{\theta}, \boldsymbol{Q}$) and two equations (Eqs. (P) and (I)). Therefore, four constitutive equations are needed to close the system of field equations defining a thermodynamic process. The four constitutive equations mathematically define the material. For a material with memory that relaxes on a material time scale [16], one possible set of constitutive equations is [9, 13]

$$\Psi = \Psi(t) = \mathfrak{P}_{s=0}^{s=t} \Big\{ \mathbf{\epsilon}(s), \mathbf{\theta}(s), a(s); \mathbf{\epsilon}(t), \mathbf{\theta}(t) \Big\},$$
(3.1)

$$\boldsymbol{\Sigma} = \boldsymbol{\Sigma}(t) = \mathop{\mathfrak{S}}_{s=0}^{s=t} \Big\{ \boldsymbol{\varepsilon}(s), \boldsymbol{\theta}(s), \boldsymbol{a}(s); \boldsymbol{\varepsilon}(t), \boldsymbol{\theta}(t) \Big\},$$
(3.2)

$$\boldsymbol{\eta} = \boldsymbol{\eta}(t) = \prod_{s=0}^{s=t} \left\{ \boldsymbol{\varepsilon}(s), \boldsymbol{\theta}(s), \boldsymbol{a}(s); \boldsymbol{\varepsilon}(t), \boldsymbol{\theta}(t) \right\},$$
(3.3)

$$\boldsymbol{Q} = \boldsymbol{Q}(\boldsymbol{C}, \boldsymbol{\theta}, \nabla \boldsymbol{\theta}), \tag{3.4}$$

where $C = F^{T} \cdot F$ is the right Cauchy-Green tensor and a(s) is the history of the shift factor that defines the material time, see Eq. (2.42). One goal of this chapter is to develop the constitutive equations listed in Eqs. (3.1) to (3.4). The Fraktur symbols in Eqs. (3.1) to (3.3) denote functionals. For materials with memory that relax on a material timescale, the constitutive functionals depend on the strain history, temperature history, and the shift factor history [13, 16].³ The constitutive functionals also take the current time *t* as a parameter argument (both to determine the current strain and temperature and to set the upper bound for the history included in the functional arguments), therefore they map the state variable histories onto a function of time.⁴

It is also useful to develop the following auxiliary constitutive equations

$$E = E(t) = \mathop{\mathfrak{E}}_{s=0}^{s=t} \left\{ \mathbf{\varepsilon}(s), \mathbf{\theta}(s), a(s); \mathbf{\varepsilon}(t), \mathbf{\theta}(t) \right\},\tag{3.5}$$

$$\boldsymbol{\chi} = \boldsymbol{\chi}(t) = \underset{s=0}{\overset{s=t}{\mathfrak{X}}} \Big\{ \boldsymbol{\varepsilon}(s), \boldsymbol{\theta}(s), \boldsymbol{a}(s); \boldsymbol{\varepsilon}(t), \boldsymbol{\theta}(t) \Big\}.$$
(3.6)

Functional forms for Eqs. (3.5) and (3.6) are not required since they E and χ can be calculated directly once all eight field variables making up a thermodynamic process have been determined.

A thermodynamic process must also obey the second law of thermodynamics. In the reference configuration, the second law is

$$\boldsymbol{\Sigma} : \dot{\boldsymbol{\varepsilon}} + \boldsymbol{\theta} \dot{\boldsymbol{\eta}} - \dot{E} - \frac{1}{\boldsymbol{\theta}} \boldsymbol{\mathcal{Q}} \cdot \nabla \boldsymbol{\theta} = \boldsymbol{\mathcal{D}} \ge 0, \tag{II}$$

where \mathcal{D} is the dissipation density (per unit volume in the reference configuration). In the next section, as we develop the constitutive equations listed in Eqs. (3.1) to (3.4), it will be shown that Eq. (II) places restrictions on the form of the constitutive equations.

3.3. Thermodynamically consistent constitutive equations for materials with memory that relax on a material timescale

In this section, we develop constitutive equations for materials with memory that relax on a material timescale, subject to the restrictions imposed by the second law of thermodynamics, Eq. (II). Four constitutive relations need to be defined to close the system of equations that define a thermodynamic process, see Eqs. (3.1) to (3.4). First, the general theory will be developed in Section 3.3.1. The results from the general theory are then applied to develop specific constitutive

³These are not the most general set of dependencies possible; we are starting pragmatically from the (well justified) dependencies already adopted in the Spectacular model implementation. For example, it is a well-known result of continuum thermodynamics that the state functions (i.e., $\Psi, \Sigma, \eta, E, \chi$) cannot depend on the temperature gradient [13], which has already been taken into account in Eqs. (3.1) to (3.3). See Ref. [13] for a derivation of the constitutive equations that starts from the theory of equipresence.

⁴Rigorously, Eqs. (3.1) to (3.4) are also functions of position X. However, constitutive models are typically concerned with solving equations in the time domain while the spatial domain is left to the finite element code. Therefore, the argument X is suppressed in the theory presented here.

equations for the Spectacular model in Section 3.3.2. Auxiliary constitutive equations for the internal energy and enthalpy according to Eqs. (3.5) and (3.6) are briefly discussed in Section 3.3.3.

The theory presented here sacrifices mathematical rigor in order to provide more intuitive explanations. Specifically, discussions of functionals and functional derivatives are omitted, although such mathematical objects are foundational for the integral form of viscoelasticity [15]. More rigorous treatments on the subject can be found in Refs. [13, 16].

3.3.1. General theory

Let us now deduce the restrictions placed on the constitutive equations by the second law of thermodynamics. Rewriting Eq. (II) in terms of the Helmholtz free energy produces

$$\boldsymbol{\Sigma} : \dot{\boldsymbol{\varepsilon}} - \dot{\Psi} - \eta \dot{\boldsymbol{\theta}} - \frac{1}{\theta} \boldsymbol{\mathcal{Q}} \cdot \nabla \boldsymbol{\theta} = \boldsymbol{\mathcal{D}} \ge 0.$$
(3.7)

The the material time derivative for the free energy is

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}} + \frac{\partial \Psi}{\partial \theta} \dot{\boldsymbol{\theta}} + \frac{\partial \Psi}{\partial t}.$$
(3.8)

Plugging Eq. (3.8) into Eq. (3.7), the expression for the second law becomes

$$\left(\boldsymbol{\Sigma} - \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}}\right) : \dot{\boldsymbol{\varepsilon}} + \left(-\eta - \frac{\partial \Psi}{\partial \theta}\right) \dot{\boldsymbol{\theta}} + \frac{\partial \Psi}{\partial t} - \frac{1}{\theta} \boldsymbol{\mathcal{Q}} \cdot \nabla \boldsymbol{\theta} = \boldsymbol{\mathcal{D}} \ge 0.$$
(3.9)

In order to satisfy the inequality in Eq. (3.9) for an arbitrary thermo-mechanical path, the terms gathered within the parentheses must vanish. Consequently, the constitutive relations for the stress and entropy must be

$$\boldsymbol{\Sigma} = \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}},\tag{3.10}$$

$$\eta = -\frac{\partial \Psi}{\partial \theta}.\tag{3.11}$$

Now, the dissipation inequality reduces to

$$\mathcal{D}_{\mathrm{TM}} - \frac{1}{\theta} \boldsymbol{\mathcal{Q}} \cdot \nabla \theta = \mathcal{D} \ge 0, \qquad (3.12)$$

where

$$\mathcal{D}_{\rm TM} \coloneqq \frac{\partial \Psi}{\partial t}.\tag{3.13}$$

The quantity \mathcal{D}_{TM} is now seen to represent the dissipation due to thermo-mechanical effects (that is, the dissipation excluding that which is due to heat flow). The inequality requires $\mathcal{D}_{\text{TM}} \ge 0$, which places restrictions on the form of the relaxation functions; these requirements are discussed elsewhere, see the original PEC/SPEC papers [5, 6, 7] and the book *Theory of Viscoelasticity* by Christensen [12] (the restrictions are hinted at in Eqs. (2.10) and (2.11)). Satisfaction of the inequality $\mathcal{D}_{\text{TM}} \ge 0$ also requires that the shift factor is always greater than zero; a > 0 [16].

3.3.2. Constitutive equations for the Spectacular model

According to Eqs. (3.10) and (3.11), equations for the stress and entropy follow from the Helmholtz free energy. Accordingly, only two independent closure relations need specification; the free energy Ψ and the heat flux Q. In this section, equations for Ψ and Q are prescribed for Spectacular, and equations for the stress and entropy are derived.

Helmholtz free energy, stress, and entropy. The Spectacular Helmholtz free energy begins with a power series expansion for functionals [14, 16], sometimes referred to as a Fréchet expansion [5]. The steps for performing the expansion are omitted here, but details can be found in Refs. [14, 16, 5, 4]. The Helmholtz free energy for the Spectacular model uses a Fréchet expansion through second-order terms and its expression is⁵

$$\Psi(t) = \Psi_{\infty}(\mathbf{\epsilon}, \theta) + \frac{1}{2} K_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du + G_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \frac{d\mathbf{\epsilon}}{ds} : \frac{d\mathbf{\epsilon}}{du} ds du - L_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du - \frac{C_D(\theta)}{2\theta_{\text{ref}}} \int_0^t \int_0^t f_4(t^* - s^*, t^* - u^*) \frac{d\theta}{ds} \frac{d\theta}{du} ds du.$$
(3.14)

The equilibrium terms in the Helmholtz free energy are a Taylor expansion in strain and temperature through second-order terms;

$$\Psi_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) = \frac{1}{2} K_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) I_{1}^{2} + G_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) \boldsymbol{e} : \boldsymbol{e} - L_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) (\boldsymbol{\theta} - \boldsymbol{\theta}_{\rm sf}) I_{1} - \frac{C_{\infty}(\boldsymbol{\theta})}{2\boldsymbol{\theta}_{\rm ref}} (\boldsymbol{\theta} - \boldsymbol{\theta}_{\rm ref})^{2}.$$
(3.15)

First-order terms in Eqs. (3.14) and (3.15) vanish to ensure that the Helmholtz free energy is minimized in the equilibrium state, which is also a consequence of Eq. (II).

According to Eqs. (3.10) and (3.11), the stress is the derivative of the free energy with respect to strain and the entropy is the derivative of the Helmholtz free energy with respect to temperature. Perhaps the most straightforward method for evaluating the partial derivatives of Eq. (3.14) is to take its material time derivative and then group terms;

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}} + \frac{\partial \Psi}{\partial \boldsymbol{\theta}} \dot{\boldsymbol{\theta}} + \frac{\partial \Psi}{\partial t}, \qquad (3.16)$$

⁵Eqs. (3.14) and (3.15) are identical to Eqs. (2.6) and (2.7), but are repeated here for convenience.

where

$$\begin{aligned} \frac{\partial \Psi}{\partial \mathbf{e}} &= \frac{\partial \Psi_{\infty}}{\partial \mathbf{e}} + K_D(\mathbf{e}, \theta) \mathbf{1} \int_0^t f_1(t^* - s^*) \frac{dI_1}{ds} ds + 2G_D(\mathbf{e}, \theta) \int_0^t f_2(t^* - s^*) \frac{d\mathbf{e}}{ds} ds \\ &- L_D(\mathbf{e}, \theta) \mathbf{1} \int_0^t f_3(t^* - s^*) \frac{d\theta}{ds} ds \\ &+ \frac{1}{2} \frac{\partial K_D}{\partial \mathbf{e}} \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du \\ &+ \frac{\partial G_D}{\partial \mathbf{e}} \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \frac{d\mathbf{e}}{ds} \cdot \frac{d\mathbf{e}}{du} ds du \\ &- \frac{\partial L_D}{\partial \mathbf{e}} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du, \end{aligned}$$
(3.17)
$$&+ \frac{\partial \Psi}{\partial \theta} = \frac{\partial \Psi_{\infty}}{\partial \theta} - L_D(\mathbf{e}, \theta) \int_0^t f_3(t^* - s^*) \frac{dI_1}{ds} ds - \frac{C_D(\theta)}{\theta_{\text{ref}}} \int_0^t f_4(t^* - s^*) \frac{d\theta}{ds} ds \\ &+ \frac{1}{2} K_D^{\theta} \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du \\ &+ G_D^{\theta} \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{ds} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{dI_1}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{ds} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dI_1}{ds} \frac{d\theta}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dH_1}{ds} \frac{d\theta}{du} ds du \\ &- \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \frac{dH_1}{ds} \frac{d\theta}{du} ds du, \end{aligned}$$

and

$$\frac{\partial \Psi}{\partial t} = \mathcal{D}_{\text{TM}} = -\frac{1}{2} K_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t \frac{\partial f_1(t^* - s^*, t^* - u^*)}{\partial t} \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du - G_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t \frac{\partial f_2(t^* - s^*, t^* - u^*)}{\partial t} \frac{d\mathbf{e}}{ds} : \frac{d\mathbf{e}}{du} \, ds \, du + L_D(\mathbf{\epsilon}, \theta) \int_0^t \int_0^t \frac{\partial f_3(t^* - s^*, t^* - u^*)}{\partial t} \frac{dI_1}{ds} \frac{d\theta}{du} \, ds \, du + \frac{C_D(\theta)}{2\theta_{\text{ref}}} \int_0^t \int_0^t \frac{\partial f_4(t^* - s^*, t^* - u^*)}{\partial t} \frac{d\theta}{ds} \frac{d\theta}{du} \, ds \, du.$$
(3.19)

According to Eq. (3.10),

$$\begin{split} \boldsymbol{\Sigma}(t) &= \frac{\partial \Psi}{\partial \boldsymbol{\varepsilon}} = \boldsymbol{\Sigma}_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) + K_D(\boldsymbol{\varepsilon},\boldsymbol{\theta}) \, \mathbf{1} \int_0^t f_1(t^* - s^*) \, \frac{dI_1}{ds} \, ds + 2G_D(\boldsymbol{\varepsilon},\boldsymbol{\theta}) \int_0^t f_2(t^* - s^*) \, \frac{d\boldsymbol{e}}{ds} \, ds \\ &- L_D(\boldsymbol{\varepsilon},\boldsymbol{\theta}) \, \mathbf{1} \int_0^t f_3(t^* - s^*) \, \frac{d\boldsymbol{\theta}}{ds} \, ds \\ &+ \frac{1}{2} \frac{\partial K_D}{\partial \boldsymbol{\varepsilon}} \int_0^t \int_0^t f_1(t^* - s^*, t^* - u^*) \, \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du \\ &+ \frac{\partial G_D}{\partial \boldsymbol{\varepsilon}} \int_0^t \int_0^t f_2(t^* - s^*, t^* - u^*) \, \frac{d\boldsymbol{e}}{ds} : \frac{d\boldsymbol{e}}{du} \, ds \, du \\ &- \frac{\partial L_D}{\partial \boldsymbol{\varepsilon}} \int_0^t \int_0^t f_3(t^* - s^*, t^* - u^*) \, \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du, \end{split}$$
(3.20)

$$\boldsymbol{\Sigma}_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) = \frac{\partial \Psi_{\infty}}{\partial \boldsymbol{\varepsilon}} = K_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})I_{1}\mathbf{1} + 2G_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})\boldsymbol{e} - L_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})(\boldsymbol{\theta} - \boldsymbol{\theta}_{\mathrm{sf}})\mathbf{1} + \frac{1}{2}\frac{\partial K_{\infty}}{\partial \boldsymbol{\varepsilon}}I_{1}^{2} + \frac{\partial G_{\infty}}{\partial \boldsymbol{\varepsilon}}\boldsymbol{e}:\boldsymbol{e} - \frac{\partial L_{\infty}}{\partial \boldsymbol{\varepsilon}}I_{1}(\boldsymbol{\theta} - \boldsymbol{\theta}_{\mathrm{sf}}).$$
(3.21)

According to Eq. (3.11),

$$\begin{split} \eta \left(t \right) &= -\frac{\partial \Psi}{\partial \theta} = \eta_{\infty} \left(\mathbf{\epsilon}, \theta \right) + L_{D} \left(\mathbf{\epsilon}, \theta \right) \int_{0}^{t} f_{3} \left(t^{*} - s^{*} \right) \frac{dI_{1}}{ds} ds + \frac{C_{D} \left(\theta \right)}{\theta_{\text{ref}}} \int_{0}^{t} f_{4} \left(t^{*} - s^{*} \right) \frac{d\theta}{ds} ds \\ &- \frac{1}{2} K_{D}^{\theta} \int_{0}^{t} \int_{0}^{t} f_{1} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{dI_{1}}{ds} \frac{dI_{1}}{du} ds du \\ &- G_{D}^{\theta} \int_{0}^{t} \int_{0}^{t} f_{2} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{de}{ds} : \frac{de}{du} ds du \\ &+ \frac{\partial L_{D}}{\partial \theta} \int_{0}^{t} \int_{0}^{t} f_{3} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{dI_{1}}{ds} \frac{d\theta}{du} ds du \\ &+ \frac{C_{D}^{\theta}}{2\theta_{\text{ref}}} \int_{0}^{t} \int_{0}^{t} f_{4} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{d\theta}{ds} \frac{d\theta}{du} ds du \end{split}$$
(3.22)

$$\eta_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta}) = -\frac{\partial \Psi_{\infty}}{\partial \boldsymbol{\theta}} = L_{\infty}(\boldsymbol{\varepsilon},\boldsymbol{\theta})I_{1} + \frac{C_{\infty}(\boldsymbol{\theta})}{\boldsymbol{\theta}_{\text{ref}}}(\boldsymbol{\theta} - \boldsymbol{\theta}_{\text{ref}}) - \frac{1}{2}K_{\infty}^{\boldsymbol{\theta}}I_{1}^{2} - G_{\infty}^{\boldsymbol{\theta}}\boldsymbol{\varepsilon} : \boldsymbol{\varepsilon} + \frac{\partial L_{\infty}}{\partial \boldsymbol{\theta}}I_{1}(\boldsymbol{\theta} - \boldsymbol{\theta}_{\text{sf}}) + \frac{C_{\infty}^{\boldsymbol{\theta}}}{2\boldsymbol{\theta}_{\text{ref}}}(\boldsymbol{\theta} - \boldsymbol{\theta}_{\text{ref}})^{2}.$$
(3.23)

Heat flux. An equation must be prescribed for the heat flux. Consistent with the assumption of isotropic mechanical behavior, we assume that heat conduction is likewise isotropic. The simplest choice that satisfies the entropy production inequality is Fourier's law,

$$\boldsymbol{q} = -k(\boldsymbol{\theta}) \operatorname{grad} \boldsymbol{\theta}, \tag{3.24}$$

where grad() is the gradient with respect to the current configuration $(\text{grad}\theta = (\partial\theta/\partial x_i)\hat{e}_i)$ and q is the spatial heat flux vector. The referential heat flux vector is related to its spatial counterpart through $Q = JF^{-1} \cdot q$. Hence, expressed in reference configuration quantities, Fourier's law becomes

$$\boldsymbol{Q}(\boldsymbol{C},\boldsymbol{\theta},\nabla\boldsymbol{\theta}) = -Jk(\boldsymbol{\theta})\boldsymbol{C}^{-1}\cdot\nabla\boldsymbol{\theta}, \qquad (3.25)$$

where C is the right Cauchy-Green tensor. With this choice, the heat conduction part of the dissipation inequality becomes

$$-\frac{1}{\theta}\boldsymbol{Q}\cdot\nabla\boldsymbol{\theta} = \frac{Jk(\boldsymbol{\theta})}{\theta}\left(\nabla\boldsymbol{\theta}\cdot\boldsymbol{C}^{-1}\cdot\nabla\boldsymbol{\theta}\right).$$
(3.26)

Since *C* is a symmetric, positive definite tensor, so is C^{-1} , and hence this constitutive relation complies with Eq. (II) as long as $k(\theta) \ge 0$ over the temperature range of the analysis.

3.3.3. Auxiliary constitutive equations

While the Helmholtz free energy is the most useful thermodynamic potential with which to formulate the theory, the enthalpy and internal energy are more useful for making comparisons with experiments. It is worth noting that we only want the values of these functions. We do not need their functional forms in terms of their natural variables, so there is no need to analytically perform the change of variables through the Legendre transformations. They can be determined in the code by computing the following definitions after the algorithmic constitutive update is complete. The internal energy and enthalpy can be calculated according to

$$E = \Psi + \theta \eta, \tag{3.27}$$

$$\chi = E - \Sigma : \varepsilon. \tag{3.28}$$

3.4. Heat equation

To derive the heat equation for Spectacular, first use the identity $E = \Psi + \theta \eta$ to plug Eq. (3.8) into Eq. (I) to rewrite the conservation of energy;

$$\boldsymbol{\theta}\boldsymbol{\eta} - \boldsymbol{\mathcal{D}}_{\mathrm{TM}} + \nabla \cdot \boldsymbol{Q} - r = 0. \tag{3.29}$$

The material time derivative of the entropy, Eq. (3.22), is

$$\begin{split} \dot{\eta} &= \frac{\partial \eta_{\infty}}{\partial \boldsymbol{\epsilon}} : \dot{\boldsymbol{\epsilon}} + \frac{\partial \eta_{\infty}}{\partial \boldsymbol{\theta}} \dot{\boldsymbol{\theta}} + L_D(\boldsymbol{\epsilon}, \boldsymbol{\theta}) \dot{I}_1 + \frac{C_D(\boldsymbol{\theta})}{\theta_{\text{ref}}} \dot{\boldsymbol{\theta}} \\ &- K_D^{\boldsymbol{\theta}} \dot{I}_1 \int_0^t f_1 \left(t^* - s^*\right) \frac{dI_1}{ds} \, ds - 2G_D^{\boldsymbol{\theta}} \dot{\boldsymbol{\epsilon}} : \int_0^t f_2 \left(t^* - s^*\right) \frac{d\boldsymbol{e}}{ds} \, ds \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\epsilon}} : \dot{\boldsymbol{\epsilon}} \int_0^t f_3 \left(t^* - s^*\right) \frac{dI_1}{ds} \, ds + 2\frac{\partial L_D}{\partial \boldsymbol{\theta}} \dot{\boldsymbol{\theta}} \int_0^t f_3 \left(t^* - s^*\right) \frac{dI_1}{ds} \, ds \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \dot{I}_1 \int_0^t f_3 \left(t^* - s^*\right) \frac{d\boldsymbol{\theta}}{ds} \, ds + 2\frac{C_D^D}{\theta_{\text{ref}}} \dot{\boldsymbol{\theta}} \int_0^t f_4 \left(t^* - s^*\right) \frac{d\boldsymbol{\theta}}{ds} \, ds \\ &+ \frac{\partial^2 L_D}{\partial \boldsymbol{\theta}^2} \dot{\boldsymbol{\theta}} \int_0^t \int_0^t f_3 \left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du \\ &+ \frac{\partial^2 L_D}{\partial \boldsymbol{\epsilon} \partial \boldsymbol{\theta}} : \dot{\boldsymbol{\epsilon}} \int_0^t \int_0^t f_3 \left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du \\ &+ L_D(\boldsymbol{\epsilon}, \boldsymbol{\theta}) \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \, ds + \frac{C_D(\boldsymbol{\theta})}{\theta_{\text{ref}}} \int_0^t \frac{\partial f_4 \left(t^* - s^*\right)}{\partial t} \frac{d\boldsymbol{\theta}}{ds} \, ds \\ &- \frac{1}{2} K_D^{\boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_1 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du \\ &- G_D^{\boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_2 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{d\boldsymbol{e}}{ds} : \frac{d\boldsymbol{e}}{du} \, ds \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_4 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_4 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{dI_1}{ds} \frac{d\boldsymbol{\theta}}{du} \, ds \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_4 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial L_D}{\partial \boldsymbol{\theta}} \int_0^t \int_0^t \frac{\partial f_3 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{d\theta}{ds} \, du \\ &+ \frac{\partial$$

where the equilibrium terms are

$$\frac{\partial \eta_{\infty}}{\partial \boldsymbol{\varepsilon}} = -\frac{\partial^2 \Psi_{\infty}}{\partial \boldsymbol{\varepsilon} \partial \boldsymbol{\theta}} = L_{\infty} (\boldsymbol{\varepsilon}, \boldsymbol{\theta}) \mathbf{1} - K_{\infty}^{\boldsymbol{\theta}} I_1 \mathbf{1} - 2G_{\infty}^{\boldsymbol{\theta}} \boldsymbol{e} + \frac{\partial L_{\infty}}{\partial \boldsymbol{\varepsilon}} I_1 + \frac{\partial L_{\infty}}{\partial \boldsymbol{\theta}} (\boldsymbol{\theta} - \boldsymbol{\theta}_{sf}) \mathbf{1} + \frac{\partial^2 L_{\infty}}{\partial \boldsymbol{\varepsilon} \partial \boldsymbol{\theta}} I_1 (\boldsymbol{\theta} - \boldsymbol{\theta}_{sf})$$
(3.31)

and

$$\frac{\partial \eta_{\infty}}{\partial \theta} = -\frac{\partial^2 \Psi_{\infty}}{\partial \theta^2} = \frac{C_{\infty}(\theta)}{\theta_{\text{ref}}} + 2\frac{\partial L_{\infty}}{\partial \theta}I_1 + 2\frac{C_{\infty}^{\theta}}{\theta_{\text{ref}}}(\theta - \theta_{\text{ref}}) + \frac{\partial^2 L_{\infty}}{\partial \theta^2}I_1(\theta - \theta_{\text{sf}}).$$
(3.32)

Substituting the Eq. (3.30) into Eq. (3.29) results in

$$\bar{C}\dot{\boldsymbol{\theta}} = -\nabla \cdot \boldsymbol{Q} + r + \mathcal{D}_{\mathrm{TM}} + \mathcal{C} + \boldsymbol{\theta}\mathcal{H},\tag{H}$$

where, for convenience, we have collected terms into the heat capacity-like quantity,

$$\bar{C} = \frac{C_g(\theta)}{\theta_{\text{ref}}} \theta + 2\frac{\partial L_{\infty}}{\partial \theta} I_1 \theta + 2\frac{C_{\infty}^{\theta}}{\theta_{\text{ref}}} \theta \left(\theta - \theta_{\text{ref}}\right) + \frac{\partial^2 L_{\infty}}{\partial \theta^2} I_1 \theta \left(\theta - \theta_{\text{sf}}\right) + 2\frac{\partial L_D}{\partial \theta} \theta \int_0^t f_3 \left(t^* - s^*\right) \frac{dI_1}{ds} ds + 2\frac{C_D^{\theta}}{\theta_{\text{ref}}} \theta \int_0^t f_4 \left(t^* - s^*\right) \frac{d\theta}{ds} ds + \frac{\partial^2 L_D}{\partial \theta^2} \theta \int_0^t \int_0^t f_3 \left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\theta}{du} ds du,$$
(3.33)

a heat source due to temperature-rate dependent heat capacity hereditary integrals,

$$\mathcal{C} = -\frac{C_D(\theta)}{\theta_{\text{ref}}} \theta \int_0^t \frac{\partial f_4(t^* - s^*)}{\partial t} \frac{d\theta}{ds} ds - \frac{C_D^{\theta}}{2\theta_{\text{ref}}} \theta \int_0^t \int_0^t \frac{\partial f_4(t^* - s^*, t^* - u^*)}{\partial t} \frac{d\theta}{ds} \frac{d\theta}{du} ds du, \quad (3.34)$$

and a heat source associated with thermo-mechanical entropic effects,

$$\begin{aligned} \mathcal{H} &= -L_{g}\left(\mathbf{\epsilon}, \mathbf{\theta}\right)\dot{I}_{1} + K_{\infty}^{\mathbf{\theta}}I_{1}\dot{I}_{1} + 2G_{\infty}^{\mathbf{\theta}}\mathbf{e}: \dot{\mathbf{e}} - I_{1}\frac{\partial L_{\infty}}{\partial \mathbf{\epsilon}}: \dot{\mathbf{\epsilon}} - \frac{\partial L_{\infty}}{\partial \mathbf{\theta}}\left(\mathbf{\theta} - \mathbf{\theta}_{\mathrm{sf}}\right)\dot{I}_{1} - \frac{\partial^{2}L_{\infty}}{\partial \mathbf{\epsilon}\partial \mathbf{\theta}}: \dot{\mathbf{\epsilon}}\left(\mathbf{\theta} - \mathbf{\theta}_{\mathrm{sf}}\right)\dot{I}_{1} \\ &+ K_{D}^{\mathbf{\theta}}\dot{I}_{1}\int_{0}^{t}f_{1}\left(t^{*} - s^{*}\right)\frac{dI_{1}}{ds}\,\mathrm{d}s + 2G_{D}^{\mathbf{\theta}}\dot{\mathbf{e}}: \int_{0}^{t}f_{2}\left(t^{*} - s^{*}\right)\frac{d\mathbf{e}}{ds}\,\mathrm{d}s \\ &- \frac{\partial L_{D}}{\partial \mathbf{\epsilon}}: \dot{\mathbf{\epsilon}}\int_{0}^{t}f_{3}\left(t^{*} - s^{*}\right)\frac{dI_{1}}{ds}\,\mathrm{d}s - \frac{\partial L_{D}}{\partial \mathbf{\theta}}\dot{I}_{1}\int_{0}^{t}f_{3}\left(t^{*} - s^{*}\right)\frac{d\mathbf{\theta}}{ds}\,\mathrm{d}s \\ &- \frac{\partial^{2}L_{D}}{\partial \mathbf{\epsilon}\partial \mathbf{\theta}}: \dot{\mathbf{\epsilon}}\int_{0}^{t}\int_{0}^{t}f_{3}\left(t^{*} - s^{*}, t^{*} - u^{*}\right)\frac{dI_{1}}{ds}\,\mathrm{d}g\,\mathrm{d}s\,\mathrm{d}u - L_{D}\left(\mathbf{\epsilon}, \mathbf{\theta}\right)\int_{0}^{t}\frac{\partial f_{3}\left(t^{*} - s^{*}\right)\frac{dI_{1}}{ds}\,\mathrm{d}s \\ &+ \frac{1}{2}K_{D}^{\mathbf{\theta}}\int_{0}^{t}\int_{0}^{t}\frac{\partial f_{1}\left(t^{*} - s^{*}, t^{*} - u^{*}\right)}{\partial t}\frac{dI_{1}}{ds}\frac{dI_{1}}{du}\,\mathrm{d}s\,\mathrm{d}u \\ &+ G_{D}^{\mathbf{\theta}}\int_{0}^{t}\int_{0}^{t}\frac{\partial f_{2}\left(t^{*} - s^{*}, t^{*} - u^{*}\right)}{\partial t}\frac{\mathrm{d}I_{2}}{\mathrm{d}s}\frac{\mathrm{d}s}{\mathrm{d}u} \\ &- \frac{\partial L_{D}}{\partial \mathbf{\theta}}\int_{0}^{t}\int_{0}^{t}\frac{\partial f_{3}\left(t^{*} - s^{*}, t^{*} - u^{*}\right)}{\partial t}\frac{\mathrm{d}I_{1}}{\mathrm{d}s}\frac{\mathrm{d}\theta}{\mathrm{d}u}\,\mathrm{d}s\,\mathrm{d}u. \end{aligned}$$

$$(3.35)$$

Equation (H) is a generalization of the heat equation, and is the additional PDE that must be solved in conjunction with the linear momentum balance, Eq. (P).

3.5. Computing instantaneous heat capacities

Our goal is to interrogate the instantaneous heat capacity in the model after a particular history of applied external conditions. This could be used, for instance, to simulate a DSC experiment. The place to start is the energy balance equation:

$$\dot{E} - \boldsymbol{\Sigma} : \dot{\boldsymbol{\varepsilon}} + \nabla \cdot \boldsymbol{Q} - r = 0. \tag{3.36}$$

The physical setting we are interested in is one where a small sample is in contact with a heat bath for which we control the temperature. We also control either the applied stress or the applied strain to the sample. This implies two important conditions. (i) There are no thermal gradients in the sample, so $\nabla \cdot \boldsymbol{Q} = 0$. (ii) The heat supply from the heat bath *r* can instantaneously adopt any value in order to support the temperature and stress or strain history to which we subject the sample. Rearranging Eq. (H) and using $\nabla \cdot \boldsymbol{Q} = 0$, we find that

$$r = \bar{C}\dot{\theta} - (\mathcal{D}_{\mathrm{TM}} + \mathcal{C} + \theta\mathcal{H}). \tag{3.37}$$

Equation (3.37) can be used to calculate the heat capacities.

 C_{ε} , Constant strain heat capacity per reference volume. This is the marginal quantity of heat absorbed per unit change in temperature with the strain held fixed, or mathematically,

$$C_{\mathbf{\epsilon}} = \left. \frac{r}{\dot{\theta}} \right|_{\dot{\mathbf{\epsilon}} = \mathbf{0}}.$$
(3.38)

By invoking the assumptions above, Eq. (3.37) applies, which transforms the heat capacity definition to

$$C_{\mathbf{\epsilon}} = \left[\bar{C} - \frac{1}{\dot{\theta}} \left(\mathcal{D}_{\text{TM}} + C + \theta \mathcal{H} \right) \right] \Big|_{\dot{\mathbf{\epsilon}} = \mathbf{0}}.$$
(3.39)

Each of the terms on the right-hand side of this equation is conveniently available as a state variable in the model. In order to get this version of the heat capacity, apply any desired temperature profile (which determines $\dot{\theta}$), apply boundary conditions to the sample so that no strains occur, and output the right-hand side of Eq. (3.39).

We will now show how this heat capacity calculation relates to its more common definition. When the heat flux is zero, the heat supply is found by rearranging Eq. (3.36),

$$r = \dot{E} - \mathbf{\Sigma} : \dot{\mathbf{\epsilon}}. \tag{3.40}$$

Inserting this into the definition of $C_{\mathbf{\epsilon}}$ gives

$$C_{\mathbf{\epsilon}} = \frac{\dot{E} - \mathbf{\Sigma} : \dot{\mathbf{\epsilon}}}{\dot{\Theta}} \bigg|_{\dot{\mathbf{\epsilon}} = \mathbf{0}},\tag{3.41}$$

which simplifies to

$$C_{\mathbf{\epsilon}} = \left. \frac{E}{\dot{\mathbf{\theta}}} \right|_{\dot{\mathbf{\epsilon}} = \mathbf{0}},\tag{3.42}$$
which is similar to the classical thermodynamic relation

$$C_{\mathbf{\epsilon}} = \left(\frac{\partial E(\mathbf{\epsilon}, \mathbf{\theta})}{\partial \mathbf{\theta}}\right)_{\mathbf{\epsilon}},\tag{3.43}$$

but is generalized to the case where the state of the material depends on the entire history of the thermodynamic variables, and not just their current value.

 C_{Σ} , Constant stress heat capacity per reference volume. This is the marginal quantity of heat absorbed per unit change in temperature with the stress held fixed, or mathematically,

$$C_{\Sigma} = \frac{r}{\dot{\theta}} \bigg|_{\dot{\Sigma} = 0}$$
(3.44)

Making use of the assumptions above gives

$$C_{\Sigma} = \left[\bar{C} - \frac{1}{\dot{\theta}} \left(\mathcal{D}_{\text{TM}} + \mathcal{C} + \theta \mathcal{H} \right) \right] \Big|_{\dot{\Sigma} = \mathbf{0}}.$$
(3.45)

This relation is nearly identical to the relation for the constant volume heat capacity Eq. (3.39), except that the applied boundary conditions must be such that the stress state is held constant. To put it another way, the same output function request is made to Sierra/SM to get the constant volume heat capacity or the constant stress heat capacity, but the external boundary conditions determine which version of the heat capacity is measured.

Unsurprisingly, this relation can also be cast in a form that approaches classical thermodynamics. Let us introduce the enthalpy density $\chi = E - \Sigma : \varepsilon$. Then

$$\dot{\boldsymbol{\chi}} + \dot{\boldsymbol{\Sigma}} : \boldsymbol{\varepsilon} = \dot{E} - \boldsymbol{\Sigma} : \dot{\boldsymbol{\varepsilon}}. \tag{3.46}$$

This lets us write

$$C_{\Sigma} = \frac{1}{\dot{\theta}} \left(\dot{\chi} + \dot{\Sigma} : \boldsymbol{\epsilon} \right) \Big|_{\dot{\Sigma} = \boldsymbol{0}}, \qquad (3.47)$$

or upon simplification

$$C_{\Sigma} = \frac{\dot{\chi}}{\dot{\theta}} \bigg|_{\dot{\Sigma} = \mathbf{0}},\tag{3.48}$$

which is reminiscent of the well-known relation

$$C_{\Sigma} = \left(\frac{\partial \chi(\Sigma, \theta)}{\partial \theta}\right)_{\Sigma}.$$
(3.49)

Again, the relation Eq. (3.48) is suitably generalized for a material with memory.

Variable	State variable name in Sierra/SM
$\overline{J^{-1}ar{C}}$	THERMAL_INERTIA
$J^{-1}\mathcal{D}_{\mathrm{TM}}$	PDISS_TOT
$J^{-1}\mathcal{C}$	HEATCAP_SRC
$J^{-1} heta \mathcal{H}$	ENTROPIC_SRC
$J^{-1}\left(\mathcal{D}_{\mathrm{TM}}+\mathcal{C}+\boldsymbol{\theta}\mathcal{H}\right)$	SRC_TOT

Table 3-1 State variables for calculating heat capacities.

Calculating the heat capacities from state variables. As stated earlier, the quantities needed to compute the heat capacities are recorded as state variables in the Spectacular model. The names of these state variables are given in Table 3-1. There is one caveat: the variables given in Eq. (3.39) and Eq. (3.45) are densities per unit volume in the *reference* configuration, and hence C_{Σ} and C_{ε} as given above are also heat capacities per unit volume in the reference configuration. However, the quantities that the Spectacular model outputs in the table above are actually given per unit volume in the *current* configuration. This choice is made in anticipation of interfacing with Aria, which uses the current configuration. In any case, values relative to the reference configuration can be obtained by multiplying model outputs by $J = \det F$.

To compare C_{Σ} and C_{ε} with experiments, they need to be converted to heat capacities per mass, in which case they should be divided by the initial density ρ_0 . In other words, C_{Σ}/ρ_0 and C_{ε}/ρ_0 are usually suitable to comparisons with the output from DSC experiments.

4. IMPLEMENTATION

This chapter describes how Spectacular is numerically integrated across a discrete timestep from t_n to t_{n+1} . Spectacular depends on the histories of three state variables: $\mathbf{\varepsilon}(s)$, $\theta(s)$, and a(s). Since $\mathbf{\varepsilon}(t_{n+1})$ and $\theta(t_{n+1})$ are passed into the model by the finite element code, the main challenge of numerically integrating the model is solving for the shift factor at the new time, $a(t_{n+1})$. The shift factor a(t) depends on $N(t) = \Re{\{\mathbf{\varepsilon}(s), \theta(s), a(s); \mathbf{\varepsilon}, \theta\}}$, which itself depends on the shift factor history a(s) through the hereditary convolution integrals that relax according to the material time $a dt^* = dt$, see Eqs. (2.42), (2.43) and (2.46). Related to the challenge of solving for log *a* is updating the hereditary integrals without explicitly saving the entire state variable histories and re-integrating over those histories at each new timestep, which would require a prohibitive amount of computational memory.

The implicit equation for the shift factor is solved using the Newton-Raphson [23] method with a midpoint integration scheme. Once the shift factor and hereditary integrals have been updated at the new timestep, all other quantities in the model are easily calculated using expressions that appear in Chapters 2 and 3.

In this chapter, values at t_n and t_{n+1} are denoted with subscripts n and n+1, respectively. Newton-Raphson iterations are denoted using superscripts, with k being the current iteration and k+1 being the next iteration. When subscripts and superscripts become too cluttered, they may be separated by a vertical bar.

4.1. Updating the hereditary integrals

Before describing the full Newton-Raphson algorithm, it is useful to first understand how the hereditary integrals are updated from time t_n to t_{n+1} . As far as numerical integration is concerned, there are four types of hereditary integrals that appear in the model. The first and second types are single and double hereditary convolution integrals that use a relaxation function as a kernel. The third and fourth types are single and double hereditary integrals that use the partial time derivative of a relaxation as the kernel. Each type of hereditary integral is discussed individually in Sections 4.1.1 to 4.1.4.

4.1.1. Single hereditary integrals

The single hereditary integrals in the model take the general form

$$\int_0^t f_r \left(t^* - s^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s,\tag{4.1}$$

where $\xi(s)$ represents a generic state variable history, which in Spectacular could be the history of the volume strain, deviatoric strain, or temperature; $\xi \in \{I_1, e, \theta\}$. The relaxation functions f_r are

defined as sums of Prony series, see Eq. (2.56), so it is convenient to express Eq. (4.1) as the sum of hereditary integrals over single Prony terms;

$$\int_{0}^{t} f_{r}(t^{*} - s^{*}) \frac{d\xi}{ds} ds = \int_{0}^{t} \sum_{p=1}^{P_{r}} w_{rp} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$
$$= \sum_{p=1}^{P_{r}} w_{rp} \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$
$$= \sum_{p=1}^{P_{r}} w_{rp} J_{rp}^{\xi}, \qquad (4.2)$$

where

$$J_{rp}^{\xi} \coloneqq \int_0^t \exp\left(-\frac{t^* - s^*}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \mathrm{d}s.$$
(4.3)

If all J_{rp}^{ξ} are known at t_{n+1} , then the single hereditary integrals can be calculated by the weighted sum in Eq. (4.2). The time derivative of J_{rp}^{ξ} is found by application of the Leibniz integral rule for differentiating under the integral sign. The result is

$$\frac{\mathrm{d}J_{rp}^{\xi}}{\mathrm{d}t} = -\frac{1}{a\tau_{rp}}J_{rp}^{\xi} + \frac{\mathrm{d}\xi}{\mathrm{d}t}.$$
(4.4)

The steps used to apply the Leibniz rule are shown in Appendix C. The two terms in Eq. (4.4) reveal that J_{rp}^{ξ} changes from the fading memory of past history and also input from new history, where the latter of which does not decay in the limit of an infinitesimally small timestep. For a midpoint Euler scheme, J_{rp}^{ξ} is updated according to

$$J_{rp}^{\xi}\Big|_{n+1} = J_{rp}^{\xi}\Big|_{n} + (t_{n+1} - t_n) \left. \frac{\mathrm{d}J_{rp}^{\xi}}{\mathrm{d}t} \right|_{n+1/2}.$$
(4.5)

To write the expression for updating J_{rp}^{ξ} in terms of values at t_n and t_{n+1} , plug Eq. (4.4) into Eq. (4.5),

$$J_{rp}^{\xi}\Big|_{n+1} = J_{rp}^{\xi}\Big|_{n} + (t_{n+1} - t_n) \left(-\frac{1}{a_{n+1/2}\tau_{rp}} J_{rp}^{\xi}\Big|_{n+1/2} + \frac{\xi_{n+1} - \xi_n}{t_{n+1} - t_n} \right),$$
(4.6)

$$J_{rp}^{\xi}\Big|_{n+1} = J_{rp}^{\xi}\Big|_{n} + (t_{n+1} - t_n) \left(-\frac{1}{a_{n+1/2}\tau_{rp}} \cdot \frac{1}{2} \left(J_{rp}^{\xi}\Big|_{n+1} + J_{rp}^{\xi}\Big|_{n} \right) + \frac{\xi_{n+1} - \xi_n}{t_{n+1} - t_n} \right),$$
(4.7)

then rearrange to solve for $J_{rp}^{\xi}\Big|_{n+1}$,

$$J_{rp}^{\xi}\Big|_{n+1} = J_{rp}^{\xi}\Big|_{n} \left(\frac{2\left(a_{n+1/2}\right)\tau_{rp} - (t_{n+1} - t_{n})}{2\left(a_{n+1/2}\right)\tau_{rp} + (t_{n+1} - t_{n})} \right) + \frac{2\left(a_{n+1/2}\right)\tau_{rp}\left(t_{n+1} - t_{n}\right)}{2\left(a_{n+1/2}\right)\tau_{rp} + (t_{n+1} - t_{n})} \frac{\xi_{n+1} - \xi_{n}}{t_{n+1} - t_{n}}, \quad (4.8)$$

where

$$a_{n+1/2} = \frac{1}{2} \left(a_{n+1} + a_n \right). \tag{4.9}$$

The reason for defining the relaxation functions as sums of Prony series is now apparent. The use of a Prony series allows the hereditary integrals to be incrementally updated based entirely on state variables at the current timestep t_n and next timestep t_{n+1} . This circumvents the need to store in memory the entire histories of $\xi(s)$ and a(s) to evaluate the hereditary integral.

However, there is a numerical issue with Eq. (4.8) when $2(a_{n+1/2})\tau_{rp} - (t_{n+1} - t_n) < 0$, which commonly occurs at high temperatures when $a_{n+1/2}$ is very small (i.e., the material is relaxing quickly). When $2(a_{n+1/2})\tau_{rp} - (t_{n+1} - t_n) < 0$, the numerator of the first term associated with the decay of $J_{rp}^{\xi}\Big|_{r}$ changes from positive to negative, possibly giving a negative value for $J_{rp}^{\xi}\Big|_{n+1}$, which is not a valid evaluation of the hereditary integral. The intuitive explanation for this occurrence is that relaxation times are faster than the timestep so that the hereditary integrals are decaying to zero at time t_{relaxed} somewhere in-between t_n and t_{n+1} , i.e., $t_n < t_{\text{relaxed}} < t_{n+1}$. However, because this numerical integration scheme assumes linear behavior over a single timestep, the algorithm, without modification, is extrapolating the rapid decay to zero at $t_{relaxed}$ to give a negative value of the integral at t_{n+1} . To prevent this spurious evaluation of the Prony integrals, the instances of $t_{n+1} - t_n$ in Eq. (4.8) are replaced with $\Delta t = \min \{ t_{n+1} - t_n, 2(a_{n+1/2})\tau_{rp} \},$ which correctly limits the decay of the memory term to zero when $a_{n+1/2}$ is very small. The exception to this replacement is the $t_{n+1} - t_n$ term appearing as the denominator of $(\xi_{n+1} - \xi_n)/(t_{n+1} - t_n)$. This term is unchanged because it is related to the input of new history rather than the fading memory of previous history. After this heuristic modification, the final expression for updating J_{rp}^{ζ} across the timestep is

$$J_{rp}^{\xi}\Big|_{n+1} = J_{rp}^{\xi}\Big|_{n} \left(\frac{2\left(a_{n+1/2}\right)\tau_{rp} - \Delta t}{2\left(a_{n+1/2}\right)\tau_{rp} + \Delta t}\right) + \frac{2\left(a_{n+1/2}\right)\tau_{rp}\Delta t}{2\left(a_{n+1/2}\right)\tau_{rp} + \Delta t}\frac{\xi_{n+1} - \xi_{n}}{t_{n+1} - t_{n}}, \qquad (4.10)$$
$$\Delta t = \min\left\{t_{n+1} - t_{n}, 2\left(a_{n+1/2}\right)\tau_{rp}\right\}.$$

4.1.2. Double hereditary integrals

The double hereditary integrals in the model take the general form

$$\int_{0}^{t} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{\mathrm{d}\xi}{\mathrm{d}s} : \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}s \,\mathrm{d}u, \tag{4.11}$$

where both $\xi(s)$ and $\phi(s)$ are generic state variable histories ($\xi, \phi \in \{I_1, e, \theta\}$) and ":" is a double contraction when ξ and ϕ are both second-order tensors (i.e., $\xi_{ij}\phi_{ij}$ following the summation convention for repeated indices) and otherwise is the scalar product. The double hereditary

integrals can also be written in terms of integrals over individual Prony terms,

$$\int_{0}^{t} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{d\xi}{ds} : \frac{d\phi}{du} ds du$$

$$= \int_{u=0}^{u=t} \int_{s=0}^{s=t} \sum_{p=1}^{P_{r}} w_{rp} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*} - u^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} : \frac{d\phi}{du} ds du$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(\int_{s=0}^{s=t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds\right) : \left(\int_{u=0}^{u=t} \exp\left(-\frac{t^{*} - u^{*}}{\tau_{rp}}\right) \frac{d\phi}{du} du\right)$$

$$= \sum_{p=1}^{P_{r}} w_{rp} J_{rp}^{\xi} : J_{rp}^{\phi}$$
(4.12)

where J_{rp}^{ξ} uses the same definition as before, see Eq. (4.3). Since the double hereditary integrals can be expressed in terms of J_{rp}^{ξ} , there is no need for a new equation to update them. Once the J_{rp}^{ξ} terms have been updated following Eq. (4.10), the double hereditary integral at the new timestep can be calculated using Eq. (4.12).

4.1.3. Single hereditary integrals with $\frac{\partial f_r(t^*-s^*)}{\partial t}$ as the kernel

Some single hereditary integrals in the model use a kernel that is a partial derivative of a relaxation function with respect to time. The general form for these integrals is

$$\int_0^t \frac{\partial f_r \left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s. \tag{4.13}$$

These integrals can also be written as a sum of Prony integrals;

$$\int_{0}^{t} \frac{\partial f_{r} \left(t^{*} - s^{*}\right)}{\partial t} \frac{d\xi}{ds} ds = \int_{0}^{t} \frac{\partial}{\partial t} \left[\sum_{p=1}^{P_{r}} w_{rp} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \int_{0}^{t} \frac{\partial}{\partial t} \left[\exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \int_{0}^{t} \frac{dt^{*}}{dt} \frac{\partial}{\partial t^{*}} \left[\exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \int_{0}^{t} \left(-\frac{1}{a\tau_{rp}}\right) \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*} - s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{1}{a\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

$$= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{y^{\xi}_{rp}}{z\tau_{rp}}\right) \frac{d\xi}{ds} ds$$

Since these integrals can be written in terms of J_{rp}^{ξ} , they can also be updated using Eq. (4.10). However, for consistency with the midpoint integration scheme, $a_{n+1/2}$ should be used to calculate their value at t_{n+1} ;

$$\int_{0}^{t_{n+1}} \frac{\partial f_r \left(t_{n+1}^* - s^* \right)}{\partial t} \frac{d\xi}{ds} \, ds = \sum_{p=1}^{P_r} w_{rp} \left(-\frac{J_{rp}^{\xi} \Big|_{n+1}}{\left(a_{n+1/2} \right) \tau_{rp}} \right). \tag{4.15}$$

4.1.4. Double hereditary integrals with $\frac{\partial f_r(t^*-s^*)}{\partial t}$ as the kernel

Some double hereditary integrals in the model use a kernel that is a partial derivative of a relaxation function with respect to time. The general form for these integrals is

$$\int_0^t \int_0^t \frac{\partial f_r \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} : \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}s \,\mathrm{d}u, \tag{4.16}$$

where, once again, ":" is a double contraction when ξ and ϕ are both second-order tensors and otherwise is the scalar product. These integrals can also be written as a sum of Prony integrals;

$$\begin{split} &\int_{0}^{t} \int_{0}^{t} \frac{\partial f_{r}\left(t^{*}-s^{*},t^{*}-u^{*}\right)}{\partial t} \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \int_{u=0}^{u=t} \int_{s=0}^{s=t} \frac{\partial}{\partial t} \left[\sum_{p=1}^{P_{r}} w_{rp} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \sum_{p=1}^{P_{r}} w_{rp} \int_{u=0}^{u=t} \int_{s=0}^{s=t} \frac{\partial}{\partial t} \left[\exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \sum_{p=1}^{P_{r}} w_{rp} \int_{u=0}^{u=t} \int_{s=0}^{s=t} \frac{dt^{*}}{dt} \frac{\partial}{\partial t^{*}} \left[\exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \right] \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \sum_{p=1}^{P_{r}} w_{rp} \int_{u=0}^{u=t} \int_{s=0}^{s=t} \left(-\frac{2}{a\tau_{rp}}\right) \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \sum_{p=1}^{P_{r}} w_{rp} \int_{u=0}^{u=t} \int_{s=0}^{s=t} \left(-\frac{2}{a\tau_{rp}}\right) \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} : \frac{d\phi}{du} \, ds \, du \\ &= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{2}{a\tau_{rp}}\right) \left(\int_{s=0}^{s=t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} \, ds \right) : \left(\int_{u=0}^{u=t} \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\phi}{du} \, ds \right) \\ &= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{2}{a\tau_{rp}}\right) \left(\int_{s=0}^{s=t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} \, ds \right) : \left(\int_{u=0}^{u=t} \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\phi}{du} \, ds \right) \\ &= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{2}{a\tau_{rp}}\right) \left(\int_{s=0}^{s=t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} \, ds \right) : \left(\int_{u=0}^{u=t} \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\phi}{du} \, ds \right) \\ &= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{2}{a\tau_{rp}}\right) \left(\int_{s=0}^{s=t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{d\xi}{ds} \, ds \right) : \left(\int_{u=0}^{u=t} \exp\left(-\frac{t^{*}-u^{*}}{\tau_{rp}}\right) \frac{d\phi}{du} \, ds \right) \\ &= \sum_{p=1}^{P_{r}} w_{rp} \left(-\frac{2}{a\tau_{rp}}\right) \left(\int_{s=0}^{t} \frac{d\phi}{dt} \, ds \right) \left(\int_{s=0}^{t}$$

Since these integrals can be written in terms of J_{rp}^{ξ} , they can also be updated using Eq. (4.10). However, for consistency with the midpoint integration scheme, $a_{n+1/2}$ should be used to calculate the integrals at t_{n+1} ;

$$\int_{0}^{t_{n+1}} \int_{0}^{t_{n+1}} \frac{\partial f_r \left(t_{n+1}^* - s^*, t_{n+1}^* - u^* \right)}{\partial t} \frac{d\xi}{ds} \frac{d\phi}{du} ds du = \sum_{p=1}^{P_r} w_{rp} \left(-\frac{2 \left(J_{rp}^{\xi} \Big|_{n+1} \right) : \left(J_{rp}^{\phi} \Big|_{n+1} \right)}{\left(a_{n+1/2} \right) \tau_{rp}} \right).$$
(4.18)

4.2. Newton-Raphson method

There are essentially three ingredients to the Newton-Raphson method. The first is defining the residual function for which the root is to be found, which is discussed in Section 4.2.1. The second is choosing an appropriate initial guess for the method that is reasonably close to the root, which is discussed in Section 4.2.2. The third is evaluating the derivatives of the residual function, which is discussed in Section 4.2.3.

4.2.1. Defining the residual function

The Newton-Raphson method is employed to solve for the shift factor at the end of the timestep, $\log a_{n+1}$. To this end, a residual function is formed from Eq. (2.43),

$$R_{\log a}\left(I_{1,n+1}, \boldsymbol{e}_{n+1}, \theta_{n+1}, \log a_{n+1}\right) = \begin{cases} \log a_{n+1} + \frac{C_1\left(N_{n+1} - \theta_{\text{ref}}\right)}{C_2 + N_{n+1} - \theta_{\text{ref}}}, & N_{n+1} \ge N_{\text{match}}, \\ \log a_{n+1} - A_1 - \frac{A_2}{N_{n+1}}, & N_{n+1} < N_{\text{match}}. \end{cases}$$
(4.19)

Recall that A_1 is chosen to ensure that the residual is continuous, see Eq. (2.44). The residual is not smooth at N_{match} . For a given $I_{1,n+1}$, \boldsymbol{e}_{n+1} , and θ_{n+1} , the $\log a_{n+1}$ value that satisfies $R_{\log a}(I_{1,n+1}, \boldsymbol{e}_{n+1}, \theta_{n+1}, \log a_{n+1}) = 0$ is a solution to Eq. (2.43). To evaluate the residual, an expression for N_{n+1} in terms of $J_{rp}^{\xi}\Big|_{n+1}$ is needed, which is easily obtained from Eq. (2.46);

$$N_{n+1}(I_{1,n+1}, \boldsymbol{e}_{n+1}, \log a_{n+1}) = \theta_{n+1} - C_0 \sum_{p=1}^{P_T} w_{Tp} J_{Tp}^{\theta} \Big|_{n+1} + C_3 \left(I_{1,n+1} - I_{1,ref} - \sum_{p=1}^{P_V} w_{Vp} J_{Vp}^{I_1} \Big|_{n+1} \right)$$

$$+ C_4 \sum_{p=1}^{P_2} w_{2p} J_{2p}^{\boldsymbol{e}} \Big|_{n+1} : J_{2p}^{\boldsymbol{e}} \Big|_{n+1}.$$

$$(4.20)$$

The Newton-Raphson method [23] works by evaluating a residual function and its derivative at a given point, then extrapolating the tangent line to zero to determine the next guess. For the residual in Eq. (4.19), this step is written as

$$R_{\log a}^{k} + \frac{\partial R_{\log a}}{\partial \log a_{n+1}} \bigg|^{k} \left(\log a_{n+1}^{k+1} - \log a_{n+1}^{k} \right) = 0,$$
(4.21)

where $\log a_{n+1}^k$ is the shift factor at the current iteration and $\log a_{n+1}^{k+1}$ is the value at the next iteration. The basic equation for Newton-Raphson is found by solving for $\log a_{n+1}^{k+1}$,

$$\log a_{n+1}^{k+1} = \log a_{n+1}^k - R_{\log a}^k \left(\frac{\partial R_{\log a}}{\partial \log a_{n+1}} \Big|^k \right)^{-1}.$$
(4.22)

The method converges when the residual on $\log a_{n+1}^{k+1}$ is zero within a specified tolerance. The requirements on the residual function for Newton-Raphson method to converge are not discussed here, but can be found elsewhere [23].

4.2.2. Initial guess

The initial guess is important for the convergence of the method. It is initially assumed that changes in the shift factor are small over a single timestep. Therefore, the converged value of the shift factor from the previous timestep is used as the initial guess for the current timestep;

$$\log a_{n+1}^0 = \log a_n. \tag{4.23}$$

However, sometimes the shift factor will undergo large changes over a single timestep. This is especially common when heating from deep in the glass, where the shift factor will precipitously drop as all non-equilibrium terms suddenly relax to zero. In this case, the Newton-Raphson method may not converge when using $\log a_n$ as the initial guess. However, after such an event, the material will be very close to the equilibrium state. Therefore, if the Newton-Raphson method fails once, the method is restarted using the equilibrium state as the initial guess,

$$\log a_{n+1}^0 = \log a_{\infty,n+1}.$$
 (4.24)

The expression for $\log a_{\infty,n+1}$ is found from Eqs. (4.19) and (4.20), but assuming that all $J_{rp}^{\xi} = 0$;

$$\log a_{\infty,n+1} = \begin{cases} -\frac{C_1 \left(N_{\infty,n+1} - \theta_{\text{ref}} \right)}{C_2 + N_{\infty,n+1} - \theta_{\text{ref}}}, & N_{\infty,n+1} \ge N_{\text{match}}, \\ A_1 + \frac{A_2}{N_{\infty,n+1}}, & N_{\infty,n+1} < N_{\text{match}}, \end{cases}$$
(4.25)

where

$$N_{\infty,n+1} = \theta_{n+1} + C_3 \left(I_{1,n+1} - I_{1,\text{ref}} \right).$$
(4.26)

4.2.3. Derivative of the residual function

To carry out each Newton-Raphson iteration by evaluating Eq. (4.22), the derivative of Eq. (4.19) is needed. Analytically evaluating the derivative is not difficult, but is tedious and requires several applications of the chain rule for differentiation. The derivative of Eq. (4.19) is

$$\frac{\partial R_{\log a}}{\partial \log a_{n+1}} = \begin{cases} 1 + \frac{C_1 C_2}{(C_2 + N_{n+1} - \theta_{\text{ref}})^2} \frac{\partial N_{n+1}}{\partial \log a_{n+1}}, & N_{n+1} \ge N_{\text{match}} \\ 1 + \frac{A_2}{N_{n+1}^2} \frac{\partial N_{n+1}}{\partial \log a_{n+1}}, & N_{n+1} < N_{\text{match}}. \end{cases}$$
(4.27)

The expression for $\frac{\partial N_{n+1}}{\partial \log a_{n+1}}$ is found by taking the derivative of Eq. (4.20),

$$\frac{\partial N_{n+1}}{\partial \log a_{n+1}} = -C_0 \sum_{p=1}^{P_T} w_{Tp} \frac{\partial J_{Tp}^{\theta} \Big|_{n+1}}{\partial \log a_{n+1}} - C_3 \sum_{p=1}^{P_V} w_{Vp} \frac{\partial J_{Vp}^{I_1} \Big|_{n+1}}{\partial \log a_{n+1}} + 2C_4 \sum_{p=1}^{P_2} w_{2p} \left(J_{2p}^{\boldsymbol{e}} \Big|_{n+1} \right) : \left(\frac{\partial J_{2p}^{\boldsymbol{e}} \Big|_{n+1}}{\partial \log a_{n+1}} \right).$$

$$(4.28)$$

Recall from Eq. (2.46) that $V \in \{1, 3\}$ and $T \in \{3, 4\}$ with V = 3 and T = 4 being the choices consistent with the PEC [5, 6, 7] model theory.

The derivative of $J_{rp}^{\xi}\Big|_{n+1}$ with respect to $\log a_{n+1}$ appears in Eq. (4.28), but the expression for $J_{rp}^{\xi}\Big|_{n+1}$ in Eq. (4.10) is in terms of $a_{n+1/2}$. Therefore, another application of the chain rule is required,

$$\frac{\partial J_{rp}^{\xi}\Big|_{n+1}}{\partial \log a_{n+1}} = \frac{\partial J_{rp}^{\xi}\Big|_{n+1}}{\partial a_{n+1/2}} \frac{\mathrm{d}a_{n+1/2}}{\mathrm{d}\log a_{n+1}}.$$
(4.29)

The derivative of Eq. (4.10) with respect to $a_{n+1/2}$ is

$$\frac{\partial J_{rp}^{\xi}\Big|_{n+1}}{\partial a_{n+1/2}} = \frac{4\tau_{rp}\Delta t J_{rp}^{\xi}\Big|_{n} + 2\tau_{rp}\left(\Delta t\right)^{2}\left(\frac{\xi_{n+1}-\xi_{n}}{t_{n+1}-t_{n}}\right)}{\left(2\left(a_{n+1/2}\right)\tau_{rp}+\Delta t\right)^{2}}.$$
(4.30)

Equation (4.30) assumes that Δt is not a function of $a_{n+1/2}$, although that is not always true, see Eq. (4.10) and the arguments in Section 4.1.1. Finally, the second term in Eq. (4.29) simplifies to

$$\frac{da_{n+1/2}}{d\log a_{n+1}} = \frac{d}{d\log a_{n+1}} \left(\frac{1}{2} \left(a_{n+1} + a_n \right) \right) \\
= \frac{1}{2} \frac{da_{n+1}}{d\log a_{n+1}} \\
= \frac{1}{2} \left(\frac{d\log a_{n+1}}{da_{n+1}} \right)^{-1} \\
= \frac{1}{2} \left(\frac{1}{a_{n+1} \ln 10} \right)^{-1} \\
= \frac{\ln 10}{2} a_{n+1}.$$
(4.31)

5. VERIFICATION

5.1. Introduction

In this chapter, parts of the Spectacular model are verified by comparing model output to analytical solutions. However, Spectacular's implicit material clock severely limits the combinations of parameters and thermo-mechanical histories for which analytical, closed-form solutions exist. To sidestep this difficulty, rigorous verification is suported with qualitative "sanity checks" of the constitutive behavior. Hopefully, the qualitative checks will be supported or replaced in the near future with more rigorous verification.

Two verification exercises and two sanity checks are presented here. In Section 5.2, the relationship between $\log a$ and N is verified under traction-free cooling and heating at a constant temperature rate. An isothermal aging period in-between the cooling and heating periods is used to verify that the shift factor relaxes to the correct equilibrium value. The parameters for this exercise where chosen to check that the piecewise shift factor equation correctly switches between its WLF and Arrhenius parts. Previous model forms exhibited "infinite aging" of the yield stress, where the yield stress continued to increase under isothermal aging long after the experimental yield stress had stopped changing [3]. One reason for implementing the Arrhenius shift factor was to limit the equilibrium shift factor at temperatures below the glass transition, and thereby eliminate infinite aging. To this end, it is demonstrated in Section 5.3 that the new Arrhenius shift factor can be used to adjust the time at which the yield stress stops evolving under isothermal aging. Although not truly a verification exercise, this demonstration shows that the new model form addresses previously identified model form errors. Another qualitative exercise is shown in Section 5.4, where the new strain hardening terms are used to stabilize tensile creep. This addresses another previously identified model form error for PEC-family models, where tensile creep results in infinite strain rates at unrealistically low creep stresses [24]. Finally, a rigorous verification of all constitutive and thermo-mechanical equations is shown in Section 5.5 for the case when the material clock is deactivated, the strain is fixed at zero, and the temperature rate is constant.

Verification tests used for the UNIVERSAL_POLYMER model have also been applied to Spectacular and are incorporated into the Sierra test repos. For more details on the UNIVERSAL_POLYMER model verification, see the LAMÉ manual [10]

5.2. Shift factor during a stress-free cool-hold-reheat cycle

The piecewise material clock was verified using a cool-hold-reheat cycle under free expansion (traction-free boundary conditions). Simulations were conducted in Sierra/SM using a single 8-node hexahedral element (hex8). A uniform temperature field was applied that started at 120 °C, was cooled to 75 °C at 1 °C/min, held constant at 75 °C for one year, then reheated back to 120 °C at 1 °C/min. The extremely long holding time was chosen to allow the shift factor to acheive its equilibrium value. Model parameters for the verification exercise are listed in Table 5-1. The temperature cycle was simulated twice: once using the piecewise Arrhenius–WLF

Name	Symbol	Value	Units
BULK GLASSY 0	K_g^{ref}	5	GPa
BULK RUBBERY 0	$K_{\infty}^{\mathrm{ref}}$	5	GPa
VOLCTE GLASSY 0	α_g^{ref}	500	$10^{-6}/{ m K}$
VOLCTE GLASSY 1	α_{g}^{Θ}	1	$10^{-6}/{\rm K}^2$
VOLCTE RUBBERY 0	α_{∞}^{ref}	500	$10^{-6}/{ m K}$
VOLCTE RUBBERY 1	$lpha_\infty^ heta$	1	$10^{-6}/{ m K}^2$
REFERENCE TEMPERATURE	θ_{ref}	373.15	Κ
STRESS FREE TEMPERATURE	θ_{sf}	393.15	Κ
WLF C1	\hat{C}_1	10	-
WLF C2	\hat{C}_2	50	-
EACT ON R	E_a/R	60 000	Κ
TMATCH WLF ARH	θ_{match}	363.15	Κ
CLOCK C3	C_3	1000	Κ
RELAX_TIME1	τ_{1p}	{1}	S
F1	w_{1p}	{1}	-
RELAX_TIME3	τ_{3p}	$\{10^{-6}\}$	S
F3	<i>w</i> _{3<i>p</i>}	{1}	_
RELAX_TIME4	τ_{4p}	$\{10^{-6}\}$	S
F 4	w_{4p}	{1}	_

Table 5-1 Parameters used to verify the piecewise shift factor function under a stress-free cool-hold-heat cycle. Unlisted parameters are either irrelevant to this thermo-mechanical history, assume their default value, or are zero.

shift factor and once using the WLF-only shift factor. To verify the implementation of the shift factor equation, the value of N was output from the model and used to analytically calculate $\log a$ using Eq. (2.43). The value of $\log a$ was also output from the model was compared to the analytically calculated $\log a$. By allowing the model to equilibrate, the equilibrium $\log a$ given by Eq. (2.50) was also verified. The calculation of N itself was not verified for this particular thermo-mechanical history.

Figure 5-1a demonstrates that the relationship between N and $\log a$ has been correctly implemented in the code by comparing the shift factor calculated in the model to the shift factor calculated by Eq. (2.43). Figure 5-1b plots the shift factor from the model against temperature. Figure 5-1b also plots the equilibrium WLF and Arrhenius shift factors given by Eq. (2.50). At high temperature, the memory integrals are negligible and the model shift factor equals the equilibrium shift factor. As the model cools, the memory terms become more important as the



(a) Shift factor versus clock temperature $\ensuremath{N}.$

(b) Shift factor and equilibrium shift factor versus temperature.

Figure 5-1 (a) Verification of the shift factor as a function of the clock temperature, $\log a(N)$, which is given by Eq. (2.43). (b) Verification of the equilibrium shift factor as a function of temperature, $\log a_{\infty}(\theta)$, which is given by Eq. (2.50). Parameters for the calculations are listed in Table 5-1.

shift factor increases, causing the shift factor to lag behind the equilibrium value. If the model is cooled from the equilibriums state, the shift factor should not exceed the equilibrium shift factor. After cooling, there is an isothermal hold, during which the memory terms relax and the shift factor approaches its equilibrium value. For the Arrhenius case, the shift factor reaches its equilibrium value during the one-year hold. The equilibrium WLF shift factor is much higher, and therefore the WLF-only model did not reach equilibrium after the simulated one-year hold.

Experimentally, the shift factor is commonly reported as a function of temperature. For this reason, it is useful for the model to accept parameters that define the shift factor equation in temperature space, then, inside the model, convert the temperature-based parameters to parameters defining the shift factor as a function of *N*. We name the hypothetical experimentally measured shift factor function as $\log \hat{a}(\theta)$. Its expression is given in Eq. (2.48). To reduce the Spectacular shift factor to a function of temperature, consider the equilibrium shift factor under free expansion $\log a_{\infty}(\theta)$, the expression for which is given in Eq. (2.50). The parameters defining $\log \hat{a}(\theta)$ (which are $\hat{C}_1, \hat{C}_2, E_a/R, \theta_{match}$) can be converted to the parameters defining $\log a_{\infty}(\theta)$ (which are C_1, C_2, A_2, N_{match}) using Eqs. (2.51) to (2.53) and (2.55). This conversion is approximate, but is very accurate for the example illustrated in Fig. 5-2, which uses the parameters listed in Table 5-1.

5.3. Using the Arrhenius Sub–Glass Transition Shift Factor to Predict the Equilibrium Yield Stress After Isothermal Aging

The piecewise Arrhenius–WLF shift factor was implemented to limit the extent of physical aging below the glass transition temperature. In previous work at Sandia [3], SPEC was used to predict yield stress evolution after isothermal aging at 55 °C for 828/DEA. Experiments found that the yield stress reached an equilibrium value at around 1000 h. In contrast, SPEC predicted that the



Figure 5-2 Demonstration of converting from shift factor expressed as a function of temperature to the equilibrium shift factor expressed as a function of $N_{\infty}(\theta)$. The expression for $\log \hat{a}(\theta)$ is shown in Eq. (2.48) and the expression for $\log a_{\infty}(\theta) = \log a(N_{\infty}(\theta))$ is shown in Eq. (2.50).

yield stress would continue to evolve for orders-of-magnitude longer than 1000 h. The WLF clock diverges, so the equilibrium shift factor is extremely high, or even poorly defined, at temperatures far below the glass transition. This allows for the yield stress to continuously evolve as the shift factor increases indefinitely. Transitioning to an Arrhenius function below the glass transition prevents the material clock from diverging. The choice of an Arrhenius form for the sub–glass transition shift factor is supported by experimental measurements of the equilibrium shift factor on a highly aged glass (20-million year old amber) [2]. Furthermore, predictions of physical aging in a KARH-type model were improved when the WLF shift factor was replaced with a piecewise Arrhenius–WLF shift factor [18].

To the authors knowledge, an Arrhenius-WLF shift factor has not been used to predict yield stress evolution. In this section, it is demonstrated that the piecewise shift factor can be used to select the time at which the yield stress stops evolving under isothermal aging. This section therefore provides no verification, but is instead a proof-of-concept to justify the sub-glass transition Arrhenius shift factor form. Predictions from Spectacular and experiments for the yield stress evolution are compared in Fig. 5-3. Details of the experiments and simulations can be found in Refs. [3, 1]. Figure 5-3a shows predictions of the yield stress evolution using a WLF-only shift factor and parameters that originally appeared in Table 5-5 of Ref. [1] (Figure 5-3a also appeared in Ref. [1] as Figure 5-24d). Although the slope of the yield stress versus aging time in Fig. 5-3a is initially correct, the yield stress continues to evolve past the time at which the experimental yield stress is constant. In Fig. 5-3b, the model parameters are modified to use the Arrhenius-WLF shift factor form with an activation energy chosen such that the yield stress stops evolving around 1000 h. The parameters used for the simulations in Fig. 5-3b are listed in Appendix D. Adding the Arrhenius piece to the clock also changed the yield stress without changing any other parameters. The clock form is tightly coupled to nearly all model responses and therefore changing the clock necesitates a new model calibration. The activation energy required to get the model to equilibrate at a time comparable to experimental measurements of the



Figure 5-3 Compressive yield stress after isothermal aging of 828/DEA for experiments (triangles) and Spectacular predictions (squares). (a) Predictions using the parameters given in Table 5-5 of Ref. [1]. (b) Predictions that modify the parameters from Table 5-5 of Ref. [1] to utilize the Arrhenius sub–glass transition shift factor with $E_a/R = 15000$ K and $\theta_{match} = 71^{\circ}$ C.

time-to-equilibrium use an activation energy of $E_a/R = 15000$ K. Unfortunately, this is much lower than the experimentally measured activation energy of $E_a/R = 137000$ K for 828/D400 [25]. When a more physically realistic activation energy is used, the model still takes too long to reach the equilibrium yield stress [26]. Future work should explore this discrepancy, specifically to see if it is possible to parameterize the model in such a way to get the correct equilibrium time using the experimentally measured activation energy.

5.4. Creep with strain hardening

Polymers exhibit large-strain hardening, which is key for arresting instabilities caused by post-yield softening. Neck propogation is an example of one such instability [27]. This fiscal year, strain hardening terms were added to Spectacular by introducing strain dependencies to the shear and bulk moduli. As justification for this new development, it is shown here that the strain hardening addresses a previous model deficiency where tensile creep resulted in an infinite strain rate at unrealistically low creep stresses [24]. By activating the strain hardening parameter $G_{\infty}^{I_2}$, the tensile creep is stabilized. Simulations were conducted Sierra/SM using a single 8-node hexahedral element (hex8). The simulated thermo-mechanical history begins at 85 °C in a stress-free state. The temperature is then lowered to 65 °C, at which time a small preload is applied in uniaxial compression by ramping from zero stress to 0.5 MPa at a strain rate of 0.01/min. Then, the uniaxial stress is ramped from the preload value to the creep stress at a strain rate of 0.1/min. Strain rates were converted to stress rates using the glass Young's modulus. The creep simulations used a preliminary Spectacular calibration for 828/DEA, the parameters fow which are given in Appendix E.

The creep response from Spectacular in tension and compression without any strain hardening is shown in Fig. 5-4. In compression, the creep response is stable even at 40 MPa, but the tensile



Figure 5-4 Predictions for creep in tension and compression without strain hardening.



Figure 5-5 Effect of increasing the strain hardening parameter $G_{\infty}^{I_2}$ on the tensile creep response at 14 MPa.



Figure 5-6 Temperature and volume strain histories applied for the zero-strain cooling at constant temperature rate verification problem.

response exhibits infinite strain rate within 6 h of creep for stresses as low as 13.5 MPa. The origin of this effect is related to the C_3 and C_4 terms in the clock. In compression, the C_3 term slows relaxation while the C_4 term accelerates it. In tension, both C_3 and C_4 accelerate the clock, leading to a positive feedback loop that eventually causes an infinite strain rates in the absence of strain hardening. Figure 5-5 shows the effect of increasing $G_{\infty}^{I_2}$ on the tensile creep response at 14 MPa. Even a modest value of $G_{\infty}^{I_2} = 1$ MPa is sufficient to prevent runaway creep.

5.5. Zero-strain cooling at a constant temperature rate

Thermal terms in the model were verified using a temperature sweep at a constant cooling rate and constant, zero strain. By setting $C_1 = 0$, the material clock is deactivated, which makes the model equations amenable to analytic evaluation. The verification problem used a thermo-mechanical history with fixed zero strain and a temperature profile that was cooled from $200 \,^{\circ}\text{C}$ to $-50 \,^{\circ}\text{C}$ at a constant cooling rate of $1 \,^{\circ}\text{C/min}$. The applied temperature and strain profiles are plotted in Fig. 5-6. The model parameters used for verification are listed in Table 5-2. For the Sierra/SM simulations, the temperature sweep was divided into 1000 timesteps, the target relative residual was 10^{-8} , the acceptable relative residual was 10^{-7} , the target absolute residual was 10^{-4} , and the acceptable relative residual was 10^{-3} . Sierra/SM simulations used a single 8-node, hexahedral element (hex8).

The verification problem compared output from Sierra/SM to analytical solutions for $\Psi(t)$, $\Sigma(t)$, $\eta(t)$, $\mathcal{D}_{TM}(t)$, $\overline{C}(t)$, C(t), $\mathcal{H}(t)$, $E^{\text{pot}}(t)$, and N(t). With $C_1 = 0$, the material clock is deactivated, therefore $t^* - s^* = t - s$. Since the cooling rate is constant, $d\theta/ds = \dot{\theta}$ is constant for all $s \in [0, t]$, and $d\theta/ds$ can therefore be removed from all the hereditary integrals involving temperature. The strain is fixed at $\boldsymbol{\varepsilon} = \boldsymbol{0}$, so all equilibrium and non-equilibrium terms involving either I_1 or \boldsymbol{e} are

Table 5-2 Parameters used for the verification problem of zero-strain cooling at a constant temperature rate.
Unlisted parameters are either irrelevant to the thermo-mechanical history, assume their default value, or are
zero.

Name	Symbol	Value	Units
BULK GLASSY 0	K_g^{ref}	5	GPa
BULK GLASSY 1	K_{g}^{Θ}	-40	MPa/K
BULK RUBBERY 0	$K_{\infty}^{\mathrm{ref}}$	1	GPa
BULK RUBBERY 1	$K^{m heta}_{\infty}$	-10	MPa/K
VOLCTE GLASSY 0	α_g^{ref}	200	$10^{-6}/{ m K}$
VOLCTE GLASSY 1	α_g^{Θ}	0.5	$10^{-6}/{\rm K}^2$
VOLCTE RUBBERY 0	α_{∞}^{ref}	600	$10^{-6}/{ m K}$
VOLCTE RUBBERY 1	$lpha_\infty^ heta$	0.1	$10^{-6}/{\rm K}^2$
HEAT CAPACITY GLASSY 0	C_g^{ref}	100	$kJ/(m^3\cdot K)$
HEAT CAPACITY GLASSY 1	C_g^{Θ}	0.1	$kJ/(m^3\cdot K^2)$
HEAT CAPACITY RUBBERY 0	$C^{\mathrm{ref}}_{\infty}$	1000	$kJ/(m^3\cdot K)$
HEAT CAPACITY RUBBERY 1	$C^{ heta}_{\infty}$	1	$kJ/(m^3\cdot K^2)$
REFERENCE TEMPERATURE	θ_{ref}	373.15	Κ
STRESS FREE TEMPERATURE	θ_{sf}	473.15	Κ
CLOCK C1	C_1	0	_
CLOCK C3	C_3	0	Κ
RELAX_TIME3	τ_{3p}	$\{10^{-2}, 10^0, 10^2, 10^3\}$	S
F3	<i>w</i> _{3<i>p</i>}	$\{0.2, 0.3, 0.3, 0.2\}$	_
RELAX_TIME4	$ au_{4p}$	$\{10^{-3}, 10^4\}$	S
F 4	<i>W</i> 4 <i>p</i>	$\{0.5, 0.5\}$	_

zero. Under these conditions, the Helmholtz free energy, Eq. (3.14), simplifies to

$$\Psi(t) = -\frac{C_{\infty}(\theta)}{2\theta_{\text{ref}}} (\theta - \theta_{\text{ref}})^2 - \frac{C_D(\theta)}{2\theta_{\text{ref}}} \dot{\theta}^2 \int_0^t \int_0^t f_4 (t - s, t - u) \, \mathrm{d}s \, \mathrm{d}u.$$
(5.1)

Only the diagonal terms of the stress, Eq. (3.20), are non-zero, and their expression is

$$\Sigma_{11}(t) = \Sigma_{22}(t) = \Sigma_{33}(t) = -L_{\infty}(\mathbf{\epsilon}, \mathbf{\theta})(\mathbf{\theta} - \mathbf{\theta}_{sf}) - L_D(\mathbf{\epsilon}, \mathbf{\theta})\dot{\mathbf{\theta}} \int_0^t f_3(t-s) \,\mathrm{d}s, \qquad (5.2)$$

The entropy, Eq. (3.22), simplifies to

$$\eta(t) = \frac{C_{\infty}(\theta)}{\theta_{\text{ref}}} (\theta - \theta_{\text{ref}}) + \frac{C_{\infty}^{\theta}}{2\theta_{\text{ref}}} (\theta - \theta_{\text{ref}})^2 + \frac{C_D(\theta)}{\theta_{\text{ref}}} \dot{\theta} \int_0^t f_4(t - s) \, \mathrm{d}s \\ + \frac{C_D^{\theta}}{2\theta_{\text{ref}}} \dot{\theta}^2 \int_0^t \int_0^t f_4(t - s, t - u) \, \mathrm{d}s \, \mathrm{d}u.$$
(5.3)

The thermo-mechanical dissipation, Eq. (3.19), simplifies to

$$\mathcal{D}_{\mathrm{TM}}(t) = \frac{C_D(\theta)}{2\theta_{\mathrm{ref}}} \dot{\theta}^2 \int_0^t \int_0^t \frac{\partial f_4(t-s,t-u)}{\partial t} \,\mathrm{d}s \,\mathrm{d}u.$$
(5.4)

The thermal inertia, Eq. (3.33), simplifies to

$$\bar{C}(t) = \frac{C_g(\theta)}{\theta_{\text{ref}}} \theta + 2\frac{C_{\infty}^{\theta}}{\theta_{\text{ref}}} \theta (\theta - \theta_{\text{ref}}) + 2\frac{C_D^{\theta}}{\theta_{\text{ref}}} \theta \dot{\theta} \int_0^t f_4(t - s) \, \mathrm{d}s.$$
(5.5)

The viscoelastic heat capacity source term, Eq. (3.34), simplifies to

$$\mathcal{C}(t) = -\frac{C_D(\theta)}{\theta_{\text{ref}}} \theta \dot{\theta} \int_0^t \frac{\partial f_4(t-s)}{\partial t} \, \mathrm{d}s - \frac{C_D^{\theta}}{2\theta_{\text{ref}}} \theta \dot{\theta}^2 \int_0^t \int_0^t \frac{\partial f_4(t-s,t-u)}{\partial t} \, \mathrm{d}s \, \mathrm{d}u.$$
(5.6)

The viscoelastic entropic source term, Eq. (3.35), is identically zero under constant, zero strain;

$$\mathcal{H}(t) = 0. \tag{5.7}$$

at

The potential energy, Eq. (B.2), simplifies to

$$E^{\text{pot}}(t) = \Psi + \theta \eta - L_D^{\text{ref}}(\theta_{\text{ref}} - \theta_{\text{sf}}) I_{1,\text{ref}} + \frac{C_g(\theta)}{2\theta_{\text{ref}}} (\theta - \theta_{\text{ref}})^2 + \theta_{\text{ref}} L_D^{\text{ref}} I_{1,\text{ref}} - \theta \frac{C_g(\theta)}{\theta_{\text{ref}}} (\theta - \theta_{\text{ref}}) + \theta_{\text{ref}} \frac{\partial L_D}{\partial \theta} \Big|_{\substack{\boldsymbol{\varepsilon} = \boldsymbol{0} \\ \theta = \theta_{\text{ref}}}} I_{1,\text{ref}}(\theta_{\text{ref}} - \theta_{\text{sf}}) - \theta \frac{C_g^{\theta}}{2\theta_{\text{ref}}} (\theta - \theta_{\text{ref}})^2.$$
(5.8)

The clock temperature, Eq. (2.46), simplifies to

$$N(t) = \theta - \dot{\theta} \int_0^t f_4(t-s) \, \mathrm{d}s - C_3 I_{1,\mathrm{ref}}.$$
(5.9)

Recall that the relaxation functions are parameterized using Prony series. For convenience, the Prony series form Eq. (2.56) is repeated here,

$$f_r(x,y) = \sum_{p=1}^{P_r} w_{rp \exp}\left(-\frac{x}{\tau_{rp}}\right) \exp\left(-\frac{y}{\tau_{rp}}\right).$$
(5.10)

For this Prony series representation, various integrals of the relaxation functions evaluate to

$$\int_0^t f_r(t-s) \,\mathrm{d}s = \sum_{p=1}^{P_r} \left[w_{rp} \tau_{rp} \left(1 - \exp\left(\frac{-t}{\tau_{rp}}\right) \right) \right],\tag{5.11}$$

$$\int_{0}^{t} \int_{0}^{t} f_{r}(t-s,t-u) \,\mathrm{d}s \,\mathrm{d}u = \sum_{p=1}^{P_{r}} \left[w_{rp} \tau_{rp}^{2} \left(1 - \exp\left(\frac{-t}{\tau_{rp}}\right) \right)^{2} \right], \tag{5.12}$$

$$\int_{0}^{t} \frac{\partial f_{r}(t-s)}{\partial t} \,\mathrm{d}s = \sum_{p=1}^{P_{r}} \left[-w_{rp} \left(1 - \exp\left(\frac{-t}{\tau_{rp}}\right) \right) \right],\tag{5.13}$$

$$\int_0^t \int_0^t \frac{\partial f_r(t-s,t-u)}{\partial t} \,\mathrm{d}s \,\mathrm{d}u = \sum_{p=1}^{P_r} \left[-2w_{rp} \left(1 - \exp\left(\frac{-t}{\tau_{rp}}\right) \right)^2 \right]. \tag{5.14}$$

Since the integrals of the relaxation functions are analytic expressions, Eqs. (5.1) to (5.9) are also analytic expressions.

Figure 5-7 compares the Sierra/SM and analytical calculations for $\Psi(t)$, $\mathcal{D}_{TM}(t)$, $\eta(t)$, and the diagonal components of $\Sigma(t)$. For all four quantities, good agreement is found between the computational and analytical solutions. Figure 5-8 compares the Sierra/SM and analytical calculations for $\bar{C}(t)$, C(t), and $\theta(t)\mathcal{H}(t)$. All three quantities show good agreement between the computational and analytical solutions. Figure 5-8 also verifies two different methods for calculating the constant-strain heat capacity. The first method uses Eq. (3.38), which calculates the constant-strain heat capacity by rearranging the generalized heat equation for Spectacular. For convenience, Eq. (3.38) is repeated here:

$$C_{\mathbf{\epsilon}} = \left[\bar{C} - \frac{1}{\dot{\theta}} \left(\mathcal{D}_{\text{TM}} + C + \theta \mathcal{H} \right) \right] \Big|_{\dot{\mathbf{\epsilon}} = \mathbf{0}}.$$
 (5.15)

The second method calculates the constant-strain heat capacity using a more general definition for viscoelastic materials, which first appeared in Eq. (3.42) and is repeated here for convenience:

$$C_{\mathbf{\epsilon}} = \frac{\dot{E}}{\dot{\theta}} \bigg|_{\dot{\mathbf{\epsilon}} = \mathbf{0}}.$$
(5.16)

Figure 5-8d shows that both methods produce the same result and that the computational solution is in agreement with the analytical solution. Figure 5-9 compares the Sierra/SM and analytical calculations for $E^{\text{pot}}(t)$ and N(t), both of which show good agreement between computational and analytical responses. Figure 5-9b also compares N(t) and $N^{\text{PEC}}(t)$, where $N^{\text{PEC}}(t)$ is calculated from $E^{\text{pot}}(t)$ using Eq. (B.8). Comparing $N^{\text{PEC}}(t)$ to N(t) allows direct comparisons of the PEC and SPEC material clocks, since $E^{\text{pot}}(t)$ and N(t) have differrent units. Figure 5-9b



Figure 5-7 Verification of the Helmholtz free energy and its partial derivatives during zero-strain cooling at a constant temperature rate. Parameters for the calculations are listed in Table 5-2.



Figure 5-8 Verification of the terms in the heat equation during zero-strain cooling at a constant temperature rate. Parameters for the calculations are listed in Table 5-2.



Figure 5-9 Verification of the potential energy and clock temperature during zero-strain cooling at a constant temperature rate. Parameters for the calculations are listed in Table 5-2.

shows that N(t) and $N^{\text{PEC}}(t)$ are relatively close for the thermo-mechanical history under consideration here, indicating that the simplifications for reducing $E^{\text{pot}}(t)$ to N(t) are well-justified for the present verification problem. It should be cautioned however, that N(t) and $N^{\text{PEC}}(t)$ are not always in agreement. For example, during isothermal aging under stress, N(t)and $N^{\text{PEC}}(t)$ can deviate significantly [26].

5.6. Conclusion

The Spectacular constitutive model was verified under limited conditions. In Section 5.2, the relationship between N and $\log a(N)$ was verified for the new piecewise WLF–Arrhenius shift factor function, at least under stress-free cooling. In Section 5.5, all constitutive and thermo-mechanical equations were verified for cooling at a constant temperature rate and zero strain. Qualitative checks were also executed to verify the model behaves as expected under more complicated conditions, but the qualitative checks were also strategically chosen to demonstrate how recent model developments have addressed previously identified model form errors. In Section 5.3, it was shown that the Arrhenius sub–glass transition shift factor could be adjusted so that the yield stress predicted by the model stops evolving under isothermal aging at the same time as the experimental yield stress. Previously, the lead stress evolved for timescales much longer than experimental measurements [3]. In Section 5.4, it was shown that the new strain hardening terms allowed for predictions of stable creep in tension. Previously, creep in tension was unstable even at low stresses [24].

In order to upgrade Spectacular to a production model, verification should be significantly improved. By deactivating the material clock and prescribing the strain and temperature histories, analytical solutions for the viscoelastic equations in the model are possible. This was already demonstrated in Section 5.5 for zero strain and a constant temperature rate. However, to get full coverage of the viscoelastic equations, verification under the following conditions are also recommended:

- fixed temperature and a constant I_1 rate,
- constant temperature rate and a constant I_1 rate, and
- fixed temperature and I_1 with a constant e rate (ideally checking constant rates for each e_{xy} , e_{yz} , and e_{zx} to also check for indexing errors).

The strain hardening terms also involve considerable complexity, and therefore should be analytically verified as well. This verification plan, if executed, would cover the majority of the Spectacular model.

6. USER GUIDE

Below is a template for specifying Spectacular parameters in Sierra/SM [11]. Square brackets identify optional commands [OPTIONAL COMMAND] and parenthesis show default values for optional parameters (DEFAULT VALUE). Comments begin with a #. The model parameters can be specified using any self-consistent unit system, so long as absolute temperatures are used. If CLOCK C1 and CLOCK C2 are not specified, then WLF C1 and WLF C2 must be specified instead. The Arrhenius part of the shift factor function can be defined either by specifying the pair NMATCH WLF ARH and CLOCK ARH2 or the pair TMATCH WLF ARH and EACT ON R. If no Arrhenius parameters are defined, then a WLF shift factor equation is used. The parameter STRESS FREE TEMPERATURE should be set equal to the initial temperature of the analysis and must be greater than both $\theta_{ref} - 30$ and $\theta_{ref} - C_2$, or else the model will return an error during the property check. This requirement on the starting temperature exists because the current model can only be initialized in the equilibrium state, and any real glassy material is unlikely to be near equilibrium at such a low temperature. This requirement may be revisited in the future. Each list of Prony times (RELAX_TIME*r*) must have the same length as the corresponding list of Prony weights (F*r*). If the Prony weights do not sum to one within a tolerance of 10^{-3} , then they are normalized to satisfy this requirement, i.e.,

if
$$\left(\sum_{p=1}^{P_r} w_{rp}^{\text{old}}\right) - 1 > 10^{-3}$$
, then $w_{rp} = \frac{w_{rp}^{\text{old}}}{\sum_{p=1}^{P_r} w_{rp}^{\text{old}}}$. (6.1)

BEGIN PARAMETERS FOR M	ODEL Spectacular		
#			
<pre># Unit abbreviations</pre>			
# t, time			
# L, length			
<pre># T, temperature (Use</pre>	e an absolute scale)		
<pre># p, pressure</pre>			
# E, energy			
# -, dimensionless			
#			
### Elastic constant:	s, set to glassy value	es ###	
BULK MODULUS	= <real></real>	# p	K_g^{ref}
SHEAR MODULUS	= <real></real>	# p	$G_g^{ m ref}$
#			-
### Bulk modulus ###			
BULK GLASSY 0	= <real></real>	# p	K_g^{ref}
[BULK GLASSY 1	= <real>(0.0)]</real>	# p/T	K_g^{Θ}
[BULK GLASSY 2	= <real>(0.0)]</real>	# p	$K_g^{I_1}$
[BULK GLASSY 3	= <real>(0.0)]</real>	# p	$K_g^{I_2}$
[BULK GLASSY 4	= <real>(0.0)]</real>	# p	$K_g^{I_3}$
BULK RUBBERY 0	= <real></real>	# p	$K^{ m ref}_{\infty}$
[BULK RUBBERY 1	= <real>(0.0)]</real>	# p/T	$K^{ heta}_{\infty}$
[BULK RUBBERY 2	= <real>(0.0)]</real>	# p	$K^{I_1}_{\infty}$

[BULK RUBBERY 3	=	<real>(0.0)]</real>	#	р	$K^{I_2}_{\infty}$
[BULK RUBBERY 4	=	<real>(0.0)]</real>	#	р	$K^{I_3}_{\infty}$
#					
### Shear modulus ###					
SHEAR GLASSY 0	=	<real></real>	#	р	G_g^{ref}
[SHEAR GLASSY 1	=	<real>(0.0)]</real>	#	p/T	$G_{g}^{\check{ heta}}$
[SHEAR GLASSY 2	=	<real>(0.0)]</real>	#	р	$G_g^{j_1}$
[SHEAR GLASSY 3	=	<real>(0.0)]</real>	#	р	$G_g^{l_2}$
[SHEAR GLASSY 4	=	<real>(0.0)]</real>	#	р	$G_g^{I_3}$
shear rubbery 0	=	<real></real>	#	р	$G^{\mathrm{ref}}_{\infty}$
[SHEAR RUBBERY 1	=	<real>(0.0)]</real>	#	p/T	$G^{ heta}_{\infty}$
[SHEAR RUBBERY 2	=	<real>(0.0)]</real>	#	р	$G^{I_1}_{\infty}$
[SHEAR RUBBERY 3	=	<real>(0.0)]</real>	#	р	$G^{I_2}_{\infty}$
[SHEAR RUBBERY 4	=	<real>(0.0)]</real>	#	р	$G^{I_3}_{\infty}$
#					
### Coefficient of Therma	al	Expansion ###			
VOLCTE GLASSY 0	=	<real></real>	#	1/T	α_g^{ref}
[VOLCTE GLASSY 1	=	<real>(0.0)]</real>	#	1/T^2	$\alpha_{g}^{\check{\theta}}$
VOLCTE RUBBERY 0	=	<real></real>	#	1/T	α^{ref}_{∞}
[VOLCTE RUBBERY 1	=	<real>(0.0)]</real>	#	1/T^2	α^{θ}_{∞}
#					
### Constant Volume Heat	Cá	apacity ###			
[HEAT CAPACITY GLASSY 0	=	<real>(0.0)]</real>	#	E/(L^3*T)	C_g^{ref}
[HEAT CAPACITY GLASSY 1	=	<real>(0.0)]</real>	#	E/(L^3*T^2)	C_{g}^{Θ}
[HEAT CAPACITY RUBBERY 0	=	<real>(0.0)]</real>	#	E/(L^3*T)	\tilde{C}_{∞}^{ref}
[HEAT CAPACITY RUBBERY 1	=	<real>(0.0)]</real>	#	E/(L^3*T^2)	$C_{\infty}^{\widetilde{ heta}}$
#					
### Clock parameters ###					
REFERENCE TEMPERATURE	=	<real></real>	#	Т	θ_{ref}
STRESS FREE TEMPERATURE	=	<real></real>	#	Т	θ_{sf}
[CLOCK C1	=	<real>]</real>	#	-	C_1
[CLOCK C2	=	<real>]</real>	#	Т	C_2
[WLF C1	=	<real>]</real>	#	-	\hat{C}_1
[WLF C2	=	<real>]</real>	#	Т	\hat{C}_2
[NMATCH WLF ARH	=	<real>(-1000.0)]</real>	#	Т	Nmatch
[CLOCK ARH2	=	<real>(-1.0)]</real>	#	Т	A_2
[TMATCH WLF ARH	=	<real>]</real>	#	Т	θ_{match}
[EACT ON R	=	<real>]</real>	#	Т	E_a/R
#					
### N definition ###					
[N THERMAL FUNCTION	=	<integer>(3) 4]</integer>	#	-	Т
[N VOLUME FUNCTION	=	<integer>(1) 3]</integer>	#	-	V
[CLOCK C0	=	<real>(1.0)]</real>	#	-	C_0
[CLOCK C3	=	= <real>(0.0)]</real>	#	Т	C_3
[CLOCK C4	=	= <real>(0.0)]</real>	#	Т	C_4
#					
<pre>### Relaxation functions</pre>	# 4	##			

RELAX_TIME1	= <real< th=""><th>list> #</th><th>t</th><th>τ_{1p}</th></real<>	list> #	t	τ_{1p}
F1	= <real< td=""><td>list> #</td><td>-</td><td>w_{1p}</td></real<>	list> #	-	w_{1p}
RELAX_TIME2	= <real< td=""><td>list> #</td><td>t</td><td>τ_{2p}</td></real<>	list> #	t	τ_{2p}
F2	= <real< td=""><td>list> #</td><td>-</td><td>w_{2p}</td></real<>	list> #	-	w_{2p}
RELAX_TIME3	= <real< td=""><td>list> #</td><td>t</td><td>τ_{3p}</td></real<>	list> #	t	τ_{3p}
F3	= <real< td=""><td>list> #</td><td>-</td><td>w_{3p}</td></real<>	list> #	-	w_{3p}
[RELAX_TIME4	= <real< td=""><td>list>(0.0)]#</td><td>t</td><td>τ_{4p}</td></real<>	list>(0.0)]#	t	τ_{4p}
[F4	= <real< td=""><td>list>(0.0)]#</td><td>-</td><td>W_{4p}</td></real<>	list>(0.0)]#	-	W_{4p}

END [PARAMETERS FOR MODEL Spectacular]

State variables available for output in Spectacular are listed in Tables 6-1 to 6-4. In those tables, the names given in the TELETYPE font can be used to specify output requests in Sierra/SM.

Name	Description
EPSXX	ϵ_{xx}
EPSYY	ε _{yy}
EPSZZ	ε _{zz}
EPSXY	ϵ_{xy}
EPSYZ	$\mathbf{\epsilon}_{yz}$
EPSZX	ϵ_{zx}
DETFINV	$J^{-1} = 1/\det \boldsymbol{F}$
CLOCK_TEMP_N	Ν
AEND	a
LOGA	loga
EPOT	E ^{pot}
NPEC	N ^{PEC}
LOGA_PEC	$\log a^{\text{PEC}}$
PDISS_TOT	$J^{-1}\mathcal{D}_{\mathrm{TM}}$
ENTROPIC_SRC	$J^{-1} \Theta \mathcal{H}$
HEATCAP_SRC	$J^{-1}\mathcal{C}$
SRC_TOT	$J^{-1}(\mathcal{D}_{\mathrm{TM}}+\mathcal{C}+\Theta\mathcal{H})$
THERMAL_INERTIA	$J^{-1}ar{C}$
HELMHOLTZ	$J^{-1}\Psi$
ENTROPY	$J^{-1}\eta$
INTERNAL_ENERGY	$J^{-1}\overline{E}=J^{-1}\left(\Psi+\theta\eta\right)$
ENTHALPY	$J^{-1}\boldsymbol{\chi} = J^{-1} \left(\boldsymbol{\Psi} + \boldsymbol{\theta} \boldsymbol{\eta} - \boldsymbol{\Sigma} : \boldsymbol{\varepsilon} \right)$

Table 6-1 State variables for the Spectacular model. Thermodynamic quantities.

Name	Description
SF1I1	$\int_0^t f_1\left(t^* - s^*\right) \frac{\mathrm{d}I_1}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_XX	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{xx}}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_YY	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{yy}}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_ZZ	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{zz}}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_XY	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{xy}}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_YZ	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{yz}}{\mathrm{d}s} \mathrm{d}s$
SF2HDEV_ZX	$\int_0^t f_2\left(t^* - s^*\right) \frac{\mathrm{d}e_{zx}}{\mathrm{d}s} \mathrm{d}s$
SF3I1	$\int_0^t f_3\left(t^* - s^*\right) \frac{\mathrm{d}I_1}{\mathrm{d}s} \mathrm{d}s$
SF3T	$\int_0^t f_3\left(t^* - s^*\right) \frac{\mathrm{d}\theta}{\mathrm{d}s} \mathrm{d}s$
SF4T	$\int_0^t f_4\left(t^* - s^*\right) \frac{\mathrm{d}\theta}{\mathrm{d}s} \mathrm{d}s$
SF1I1I1	$\int_{0}^{t} \int_{0}^{t} f_{1} \left(t^{*} - s^{*}, t^{*} - u^{*} \right) \frac{\mathrm{d}I_{1}}{\mathrm{d}s} \frac{\mathrm{d}I_{1}}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
SF2HDEVHDEV	$\int_0^t \int_0^t f_2 \overline{\left(t^* - s^*, t^* - u^*\right)} \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}s} : \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
SF3I1T	$\int_0^t \int_0^t f_3 \overline{(t^* - s^*, t^* - u^*)} \frac{\mathrm{d}I_1}{\mathrm{d}s} \frac{\mathrm{d}\theta}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
SF4TT	$\int_0^t \int_0^t f_4 \left(t^* - s^*, t^* - u^* \right) \frac{\mathrm{d}\theta}{\mathrm{d}s} \frac{\mathrm{d}\theta}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$

Table 6-2 State variables for the Spectacular model. Hereditary integrals.

Name	Description
SDF3I1	$\int_0^t \frac{\partial f_3\left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}I_1}{\mathrm{d}s} \mathrm{d}s$
SDF4T	$\int_0^t \frac{\partial f_4\left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}\theta}{\mathrm{d}s} \mathrm{d}s$
SDF1I111	$\int_0^t \int_0^t \frac{\partial f_1\left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{\mathrm{d}I_1}{\mathrm{d}s} \frac{\mathrm{d}I_1}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
SDF2HDEVHDEV	$\int_0^t \int_0^t \frac{\partial f_2(t^* - s^*, t^* - u^*)}{\partial t} \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}\boldsymbol{s}} : \frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}\boldsymbol{u}} \mathrm{d}\boldsymbol{s} \mathrm{d}\boldsymbol{u}$
SDF3I1T	$\int_0^t \int_0^t \frac{\partial f_3\left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{\mathrm{d}I_1}{\mathrm{d}s} \frac{\mathrm{d}\theta}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
SDF4TT	$\int_0^t \int_0^t \frac{\partial f_4 \left(t^* - s^*, t^* - u^*\right)}{\partial t} \frac{\mathrm{d}\theta}{\mathrm{d}s} \frac{\mathrm{d}\theta}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
PDISS_I1I1	$-J^{-1}\left(\frac{K_D(\boldsymbol{\epsilon},\boldsymbol{\theta})}{2}\right)\int_0^t\int_0^t\frac{\partial f_1\left(t^*-s^*,t^*-u^*\right)}{\partial t}\frac{\mathrm{d}I_1}{\mathrm{d}s}\frac{\mathrm{d}I_1}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u$
PDISS_HdevHdev	$-J^{-1}G_D(\mathbf{\epsilon}, \mathbf{\theta}) \int_0^t \int_0^t \frac{\partial f_2(t^* - s^*, t^* - u^*)}{\partial t} \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}s} : \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
PDISS_I1T	$J^{-1}L_D(\mathbf{\epsilon}, \mathbf{\theta}) \int_0^t \int_0^t \frac{\partial f_3(t^* - s^*, t^* - u^*)}{\partial t} \frac{\mathrm{d}I_1}{\mathrm{d}s} \frac{\mathrm{d}\mathbf{\theta}}{\mathrm{d}u} \mathrm{d}s \mathrm{d}u$
PDISS_TT	$J^{-1}\left(\frac{C_D(\theta)}{2\theta_{\text{ref}}}\right)\int_0^t\int_0^t\frac{\partial f_4\left(t^*-s^*,t^*-u^*\right)}{\partial t}\frac{\mathrm{d}\theta}{\mathrm{d}s}\frac{\mathrm{d}\theta}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u$

Table 6-3 State variables for the Spectacular model. Hereditary integrals with $\partial f_r(t^*)/\partial t$ kernels.

_

Name	Description
IF1I1_p	$J_{1p}^{I_1}$
IF2HDEV_XX_ p	$J_{2p}^{e_{xx}}$
IF2HDEV_YY_ p	$J_{2p}^{e_{yy}}$
IF2HDEV_ZZ_ p	$J_{2p}^{e_{zz}}$
IF2HDEV_XY_ p	$J_{2p}^{e_{xy}}$
IF2HDEV_YZ_ p	$J_{2p}^{e_{yz}}$
IF2HDEV_ZX_ p	$J_{2p}^{e_{zx}}$
IF3I1_p	$J_{3p}^{I_1}$
IF3T_p	J^{θ}_{3p}
IF4T_p	J_{4p}^{Θ}

Table 6-4 State variables for the Spectacular model. Hereditary integrals on single Prony terms.

7. CONCLUSION

A comprehensive description of the Spectacular constitutive model has been presented, including the thermo-mechanical theory, the numerical methods used to time-integrate the model, a few verification tests, and a user guide that describes the syntax for using the model in Sierra/SM. It is our hope that this document will serve as a useful reference for both users and developers of Spectacular.

Despite the broad scope of this report, there are still some aspects of the Spectacular model theory that were not included. When writing the report, priority was given to information of practical importance, information specific to Spectacular, and information not clearly documented in other sources. However, a complete theory guide for Spectacular should at least include the following topics:

- **The derivation of the Helmholtz free energy.** The viscous part of the free energy (Eqs. (2.6) and (3.14)) is a second-order Fréchet expansion, which is a Taylor series for functionals [5]. The PEC [5, 6] and SPEC [7] papers give almost no information about the general form of the Fréchet expansion; Only the final form of the free energy is given. However, more details appear in an earlier paper from the Caruthers group [16] and the general form of the Fréchet expansion appears in *Theory of Functionals and of Integral and Integro-Differential Equations* [14]. Francophones can follow the references therin to discover the original work of Maurice Fréchet. Once the free energy is written as a Fréchet expansion, first-order terms in the expansion must vanish. This is because thermodynamic constraints require that free energy is minimized at the equilibrium state [13, 16]. Finally, by considering a variety of instantaneous perturbations in strain, temperature, or strain and temperature, the physical meaning of the terms in the Fréchet expansion can be inferred (e.g., integral prefactors are related to the bulk moduli, shear moduli, CTE, constant volume heat capacity). This final step is thoroughly described in the PEC derivation paper [5].
- A discussion of stress and strain measures in the model. PEC uses the Hencky strain and its stress conjugate, while SPEC and Spectacular use the integrated unrotated rate of deformation tensor. The integrated unrotated rate of deformation tensor approximates the Hencky strain, but has a different conjugate stress tensor. More information on this can be found in the SPEC paper [7].
- A discussion on other forms for the relaxation function Prony sums. The form of the Prony sum used to define the relaxation functions (Eq. (2.56)) is only one of at least three possibilities. Other possible forms are discussed in the appendices of the PEC derivation paper [5].
- A more expansive verification section. Currently, only the thermal terms and the shift factor function $\log a(N)$ have been rigorously verified. Ideally, volume and shear terms should also be verified. Improved verification is necessary if the model is to achieve production status.
- A calibration guide. Spectacular is challenging to calibrate, both with regards to planning the experimental campaign and using the data to determine model parameters. Unfortunately, a

simple "recipe" for calibrating Spectacular is not possible, as the calibration method is specific to the available experimental data and material behaviors of interest.

A thoughtful review of efforts to validate the model. Currently, PEC, SPEC, and Spectacular offer the most complete thermodynamic descriptions for glass-forming materials. Few, if any, other models qualitatively predict volume relaxation, enthalpy relaxation, yield, strain hardening, and physical aging all within a single model framework. Nevertheless, it has proven challenging to generate a single model parameterization that represents disparate thermo-mechanical behaviors of a single material. Extensive validation efforts can be found for PEC and SPEC in Refs. [6, 28, 7, 24]. The body of validation studies for PEC-type models can be augmented using recent work on Spectacular from the authors of this report [1, 29, 26].

This list of additional content for an ideal Spectacular report also hints at future work. There are clear practical benefits for increasing the extent of the model that is verified and producing a calibration guide. Improving the verification makes the model production-worthy, and a calibration guide makes the model more accessible to analysts. Validation is a higher risk, more research focused effort, but is important for improving predictions of physical aging and pushing Sandia to the forefront of models for glass-forming materials. Although Spectacular may be one of the most comprehensive nonlinear viscoelastic models, it has still failed a number of validation tests. The validation of several broad types of polymer constitutive models is discussed in Ref. [24]. In that chapter, the SPEC model is referred to as the TVEM, and a number of issues with the model are identified in a list. Through our own work, we have also identified a number of challenging predictions for Spectacular, with some overlap with the issues identified in Ref. [24]. For example:

- For enthalpy recovery after cooling into the glass, a single parameterization for f_4 does not fit the response for all thermal histories. Generally, to predict enthalpy recovery after more extensive physical aging (i.e., a larger heat capacity spike), the model requires a broader and longer thermal relaxation function (i.e., smaller β_4 and larger τ_4) [1, 29]. However, the analyses that lead to this finding were carried out using a single element, which neglects heat diffusion and thermal gradients. It is possible that explicitly modeling thermal gradients could improve the discrepancy between simulations and experiments when predicting enthalpy recovery across multiple thermal histories with a single parameter set. Alternatively, quantities like the total recovered enthalpy or fictive temperature could be used for comparisons, as these quantities are insensitive to thermal gradients [30].
- After isothermal, no-load aging, the yield stress of glassy polymers increases [3]. Quantitatively predicting this phenomenon in Spectacular seems to require that the shear relaxation function f_2 relaxes out sooner than the thermal relaxation function f_4 . This is contrary to experiments, which find that the relaxation time for shear is longer than the volumetric or thermal relaxation times [31].
- Under isothermal aging with an applied load, the yield stress increases more quickly than under isothermal, no-load aging [32]. The origin of this phenomenon is still not clear, but Spectacular is able to predict it in a physical aging framework [26]. However, the Spectacular predictions are generally too soft (the creep strain after aging under load is too

high and the yield stress is too low). Comparisons between the simplified potential energy the potential energy have indicated that the PEC model might predict a stiffer responses, bringing predictions more in line with experiments. This may indicate that under more complicated thermo-mechanical histories, the simplified potential energy is not suitable for quantitative predictions. More investigations comparing the PEC and Spectacular responses are needed to settle this issue.

A common theme is present for each of these challenging predictions: The model can be tuned to represent a material's response for almost any thermo-mechanical path, but a single calibration is apparently unable to represent all thermo-mechanical paths. It has been suggested that the predictive capabilities of a thermo-rheologically simple model, like Spectacular, are limited [24].

The newly implemented strain hardening terms should also be validated. Currently, strain hardening is incorporated using strain-dependent integral prefactors. However, it could also be achieved using a higher order Fréchet expansion or new clock terms that slow relaxation at large strains. Without comparing and validating these three methods, one cannot determine which method is most physically realistic. In Ref. [33], it was found that both viscous and entropic (rubber elastic) effects contributed to strain hardening, so it is possible that strain hardening should be modeled as some combination of the three methods.

Although certain predictions are challenging for Spectacular, it is able to quantitatively predict an impressive array of behaviors, hinting that the model is correctly representing some underlying physics of glasses. For example, quantitative predictions emerge for the temperature sensitivity of the yield stress or the change in the yield stress after isothermal aging without directly calibrating the model to these responses. Hopefully, thoughtful study of the model form alongside creative experiments will help to inform future model development and address outstanding issues with the model.
REFERENCES

- K. N. Cundiff, K. N. Long, J. M. Kropka, S. Carroll, and C. Groves, "ASC P&EM FY21 L2 Milestone 7836: Constitutive Model Development for Aging Polymer Encapsulants," Technical Report SAND2021-11193, Sandia National Laboratories, Sept. 2021.
- [2] J. Zhao, S. L. Simon, and G. B. McKenna, "Using 20-million-year-old amber to test the super-Arrhenius behaviour of glass-forming systems," *Nature Communications*, vol. 4, p. 1783, Apr. 2013.
- [3] C. M. Tenney, K. N. Long, and J. M. Kropka, "Predictions of Yield Strength Evolution Due to Physical Aging of 828 DGEBA/DEA using the Simplified Potential Energy Clock Model," Technical Report SAND2019-2248R, Sandia National Laboratories, Feb. 2019.
- [4] S. J. Grutzik and K. N. Long, "Survey of possible strategies for adding strain hardening to SPEC model," Technical Report SAND2020-0160CTF, Sandia National Laboratories, Jan. 2020.
- [5] J. M. Caruthers, D. B. Adolf, R. S. Chambers, and P. Shrikhande, "A thermodynamically consistent, nonlinear viscoelastic approach for modeling glassy polymers," *Polymer*, vol. 45, pp. 4577–4597, June 2004.
- [6] D. B. Adolf, R. S. Chambers, and J. M. Caruthers, "Extensive validation of a thermodynamically consistent, nonlinear viscoelastic model for glassy polymers," *Polymer*, vol. 45, pp. 4599–4621, June 2004.
- [7] D. B. Adolf, R. S. Chambers, and M. A. Neidigk, "A simplified potential energy clock model for glassy polymers," *Polymer*, vol. 50, pp. 4257–4269, Aug. 2009.
- [8] B. Talamini, "Extension of SPECTACULAR constitutive model for full thermomechanical coupling," Technical Report SAND2019-12917CTF, Sandia National Laboratories, Oct. 2019.
- [9] B. Talamini and K. N. Cundiff, "Extension of SPECTACULAR constitutive model for full thermomechanical coupling," Technical Report SAND2021-9851CTF, Sandia National Laboratories, Aug. 2021.
- [10] LAMÉ Team, *Library of Advanced Materials for Engineering (LAMÉ) 5.14*. Albuquerque, NM, May 2023.
- [11] SIERRA Solid Mechanics Team, Sierra/SolidMechanics 5.14 User's Guide. Albuquerque, NM, May 2023.
- [12] R. M. Christensen, *Theory of Viscoelasticity*. Mineola, N.Y: Dover Publications, 2nd ed., 2003.
- [13] B. D. Coleman, "Thermodynamics of materials with memory," Archive for Rational Mechanics and Analysis, vol. 17, pp. 1–46, Jan. 1964.
- [14] V. Volterra, *Theory of Functionals and of Integral and Integro-Differential Equations*. New York, NY: Dover Publications, 1959.

- [15] B. D. Coleman and W. Noll, "Foundations of Linear Viscoelasticity," *Reviews of Modern Physics*, vol. 33, pp. 239–249, Apr. 1961.
- [16] S. R. Lustig, R. M. Shay, and J. M. Caruthers, "Thermodynamic constitutive equations for materials with memory on a material time scale," *Journal of Rheology*, vol. 40, pp. 69–106, Jan. 1996.
- [17] M. L. Williams, R. F. Landel, and J. D. Ferry, "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids," *Journal of the American Chemical Society*, vol. 77, pp. 3701–3707, July 1955.
- [18] L. Grassia and S. L. Simon, "Modeling volume relaxation of amorphous polymers: Modification of the equation for the relaxation time in the KAHR model," *Polymer*, vol. 53, pp. 3613–3620, July 2012.
- [19] J. E. Soussou, F. Moavenzadeh, and M. H. Gradowczyk, "Application of Prony Series to Linear Viscoelasticity," *Transactions of the Society of Rheology*, vol. 14, no. 4, 1970.
- [20] G. Williams and D. C. Watts, "Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function," *Transactions of the Faraday Society*, vol. 66, pp. 80–85, Jan. 1970.
- [21] M. Cardona, R. Chamberlin, and W. Marx, "The history of the stretched exponential function," *Annalen der Physik*, vol. 519, no. 12, pp. 842–845, 2007.
- [22] R. Kohlrausch, "Theorie des elektrischen Rückstandes in der Leidener Flasche," *Annalen der Physik und Chemie*, vol. 167, no. 2, pp. 179–214, 1854.
- [23] W. H. Press, ed., Numerical Recipes in Fortran 77: The Art of Scientific Computing, vol. 1 of Fortran Numerical Recipes. Cambridge [England]; New York: Cambridge University Press, 2nd ed ed., 1996.
- [24] G. Medvedev and J. Caruthers, "A comparison of constitutive descriptions of the thermo-mechanical behavior of polymeric glasses," in *Polymer Glasses* (C. Roth, ed.), pp. 451–536, Boca Raton, FL: CRC Press, Dec. 2016.
- [25] J. M. Kropka, S. Carroll, C. Groves, G. K. Arechederra, K. M. Wilson, G. Gabaldon, S. Comeau, and J. D. McCoy, "Physical Aging in Epoxies: Experimental Assessments," Conference Presentation SAND2023-06505C, Sandia National Laboratories, Albuquerque, NM, July 2023.
- [26] K. N. Cundiff, M. R. Buche, S. J. Grutzik, K. N. Long, and J. M. Kropka, "Physical Aging in Epoxies: Modeling," Conference Presentation SAND2023-06569C, Sandia National Laboratories, Albuquerque, NM, July 2023.
- [27] K. N. Cundiff, G. Ayoub, and A. A. Benzerga, "Modeling the viscoplastic behavior of a semicrystalline polymer," *International Journal of Solids and Structures*, vol. 254–255, p. 111920, Nov. 2022.

- [28] D. B. Adolf and R. S. Chambers, "A thermodynamically consistent, nonlinear viscoelastic approach for modeling thermosets during cure," *Journal of Rheology*, vol. 51, pp. 23–50, Jan. 2007.
- [29] K. N. Cundiff, K. N. Long, J. M. Kropka, S. Carroll, and C. Groves, "Calibration of a nonlinear viscoelastic model to predict physical aging," Conference Presentation SAND2022-11703C, Sandia National Laboratories, Albuquerque, NM, Aug. 2022.
- [30] S. Simon and G. McKenna, "Structural recovery and physical aging of polymeric glasses," in *Polymer Glasses* (C. Roth, ed.), pp. 23–54, Boca Raton, FL: CRC Press, Dec. 2016.
- [31] J. Caruthers and G. Medvedev, "Thermo-mechanical signatures of polymeric glasses," in *Polymer Glasses* (C. Roth, ed.), pp. 106–178, Boca Raton, FL: CRC Press, Dec. 2016.
- [32] M. Razavi, E. Xing, and M. D. Ediger, "Overaging with Stress in Polymer Glasses? Faster Segmental Dynamics despite Larger Yield Stress!," *Macromolecules*, vol. 55, pp. 10043–10051, Nov. 2022.
- [33] C. C. W. J. Clarijs and L. E. Govaert, "Strain hardening in glassy polymers: Influence of network density on elastic and viscous contributions," *Journal of Polymer Science Part B: Polymer Physics*, vol. 57, pp. 1001–1013, Aug. 2019.
- [34] H. Flanders, "Differentiation Under the Integral Sign," *The American Mathematical Monthly*, vol. 80, no. 6, pp. 615–627, 1973.

A. RELATING THE TANGENT AND SECANT COEFFICIENTS OF THERMAL EXPANSION

To specify the thermal strain behavior in Spectacular, the user inputs parameters that define the tangent volumetric CTEs, denoted as $\alpha_L(\theta)$, where *L* is used here as an index to represent either the instantaneous or equilibrium limiting response, i.e., $L \in \{g, \infty\}$. The tangent CTEs are defined as

$$\alpha_L(\theta) \coloneqq \frac{\mathrm{d}I_1}{\mathrm{d}\theta},\tag{A.1}$$

where $I_1(\theta)$ is a function of temperature that defines either the instantaneous (L = g) or equilibruim $(L = \infty)$ volume strain under stress-free expansion. On the other hand, the model theory for Spectacular is formulated using the secant volumetric CTEs, denoted as $\delta_L(\theta)$. The definition for the secant volumetric CTEs are

$$\alpha_L(\theta) \coloneqq \frac{dI_1}{d\theta},\tag{A.2}$$

where *L* and $I_1(\theta)$ are defined as before. The user inputs parameters to define $\alpha_L(\theta)$, which are converted to parameters defining $\delta_L(\theta)$ within the Spectacular code. This appendix shows how $\alpha_L(\theta)$ and $\delta_L(\theta)$ are related.

For both the instantaneous and equilibrium tangent CTE, the user specifies the CTE at the reference temperature α_L^{ref} and the slope of the CTE with temperature α_L^{θ} . Therefore, the tangent CTE function is

$$\alpha_L(\theta) = \alpha_L^{\text{ref}} + \alpha_L^{\theta}(\theta - \theta_{\text{sf}}).$$
(A.3)

The function can also be rewritten as an expansion about the stress-free temperature θ_{sf} , which is the temperature at which there is zero thermal strain in the equilibrium state under stress-free expansion;

$$\begin{aligned} \alpha_L(\theta) &= \alpha_L^{\text{ref}} + \alpha_L^{\theta}(\theta - \theta_{\text{ref}}) \\ &= \alpha_L^{\text{ref}} + \alpha_L^{\theta}(\theta - \theta_{\text{sf}}) + \alpha_L^{\theta}(\theta_{\text{sf}} - \theta_{\text{ref}}) \\ &= \alpha_L^{\text{sf}} + \alpha_L^{\theta}(\theta - \theta_{\text{sf}}), \end{aligned}$$
(A.4)

where

$$\alpha_L^{\rm sf} = \alpha_L^{\rm ref} + \alpha_\infty^{\theta} \left(\theta_{\rm sf} - \theta_{\rm ref} \right). \tag{A.5}$$

The expression for $\delta_L(\theta)$ in terms of the user-defined parameters (α_L^{ref} and α_L^{θ}) is found by

integrating $\alpha_L(\theta)$;

$$\begin{aligned} \frac{dI_{1}}{d\theta} &= \alpha_{L}(\theta) \\ dI_{1} &= \alpha_{L}(\theta) d\theta \\ I_{1}(\theta) &= \int_{\theta_{sf}}^{\theta} \alpha_{L}(\theta) d\theta \\ &= \int_{\theta_{sf}}^{\theta} \alpha_{L}^{sf} + \alpha_{L}^{\theta}(\theta - \theta_{sf}) d\theta \\ &= \left(\alpha_{L}^{sf} + \frac{1}{2}\alpha_{L}^{\theta}(\theta - \theta_{sf})\right) (\theta - \theta_{sf}) \\ \frac{I_{1}(\theta)}{\theta - \theta_{sf}} &= \alpha_{L}^{sf} + \frac{1}{2}\alpha_{L}^{\theta}(\theta - \theta_{sf}) \\ \delta_{L}(\theta) &= \alpha_{L}^{sf} + \frac{1}{2}\alpha_{L}^{\theta}(\theta - \theta_{sf}) . \end{aligned}$$
(A.6)

Finally, to maintain a consistent form between the functions defining all viscoelastic limits, rewrite $\delta_L(\theta)$ as a linear expansion about θ_{ref} ;

$$\begin{split} \delta_{L}(\theta) &= \alpha_{L}^{\mathrm{sf}} + \frac{1}{2} \alpha_{L}^{\theta}(\theta - \theta_{\mathrm{sf}}) \\ &= \alpha_{L}^{\mathrm{sf}} + \frac{1}{2} \alpha_{L}^{\theta}(\theta - \theta_{\mathrm{ref}}) - \frac{1}{2} \alpha_{L}^{\theta}(\theta_{\mathrm{sf}} - \theta_{\mathrm{ref}}) \\ &= \alpha_{L}^{\mathrm{ref}} + \alpha_{L}^{\theta}(\theta_{\mathrm{sf}} - \theta_{\mathrm{ref}}) + \frac{1}{2} \alpha_{L}^{\theta}(\theta - \theta_{\mathrm{ref}}) - \frac{1}{2} \alpha_{L}^{\theta}(\theta_{\mathrm{sf}} - \theta_{\mathrm{ref}}) \\ &= \alpha_{L}^{\mathrm{ref}} + \frac{1}{2} \alpha_{L}^{\theta}(\theta_{\mathrm{sf}} - \theta_{\mathrm{ref}}) + \frac{1}{2} \alpha_{L}^{\theta}(\theta - \theta_{\mathrm{ref}}) \\ &= \delta_{L}^{\mathrm{ref}} + \delta_{L}^{\theta}(\theta - \theta_{\mathrm{ref}}), \end{split}$$

where

$$\delta_L^{\text{ref}} = \alpha_L^{\text{ref}} + \frac{1}{2} \alpha_L^{\theta} \left(\theta_{\text{sf}} - \theta_{\text{ref}} \right), \qquad (A.7)$$

$$\delta_L^{\theta} = \frac{1}{2} \alpha_L^{\theta}. \tag{A.8}$$

Thus, Eqs. (2.34) and (2.35) have been proven.

B. DERIVING THE SPECTACULAR CLOCK FROM THE PEC CLOCK

The material clock (i.e., the shift factor) in the PEC model [5, 6] depends on the potential energy (i.e., configurational energy) E^{pot} . The potential energy functional for PEC was derived from the Helmholtz free energy functional and therefore had no free parameters. In the SPEC model [7], the potential energy functional was greatly simplified, then divided by a heat capacity to yield the term N, called the "clock temperature" in this report. As part of the simplification, many hereditary integrals were neglected and coefficients to integrals were made into constant, free parameters. Converting the coefficients to free parameters increased the flexibility of the calibration process, but it also separated the coefficients from their physical meaning and removed their dependence on temperature and strain. The material clock in Spectacular also depends on N, but challenging physical aging predictions have motivated a re-evaluation of the assumptions used to simplify E^{pot} to N. Essentially, Spectacular has been able to predict yield stress evolution after isothermal aging for any given aging temperature using a single parameter set, but a single parameter set has not been able to predict isothermal yield stress evolution for more than one aging temperature. It is an outstanding question if the implementation of temperature dependent clock parameters would enably physical aging predictions accross multiple temperatures, and a first step towards answering that question is studying the old PEC clock form.

The process for simplifying the potential energy is described in Adolf et al. 2009 [7], but the derivation is somewhat challenging to follow given the limited length allowed in a journal article, as well as differences in notation between PEC and SPEC⁶. This appendix thoroughly describes the process for simplifying E^{pot} into N, and also shows how to compare the shift factors based on both measures in order to assess the importance of the terms that appear in E^{pot} , but are neglected in N.

B.1. Expression for the potential energy used in the PEC clock

The potential (i.e., configurational) energy is based on the internal energy $E = \Psi + \theta \eta$, but terms related to changes in kinetic (i.e., thermal) energy are subtracted from the expression. The authors of Refs. [5, 7] argue that when the material is subjected to an infinitely fast change in temperature, the macromolecules do not have time to rearrange. Therefore, the change in internal energy from an infinitely fast quench is due to a change in the kinetic energy rather than the potential energy. If the memory and equilibrium terms in $\Psi(t)$ are well balanced, then E^{pot} can be made constant for an infinitely fast quench by replacing equilibrium terms X_{∞} multiplied by temperature with the negative difference terms $-X_D$. The authors in Refs. [5, 7] are less clear about what should be done for cross-terms involving both temperature and volume, but assert that the clock performs better when the cross-terms are also switched from X_{∞} to $-X_D$. Given these arguments, the expression for E^{pot} for the Spectacular model follows directly from the choice of $\Psi(t)$ shown in

⁶Most of the parameters in PEC are written using either Ψ or ψ with a series of subscripts. While this notation highlights the elegance of deriving the entire model from a Fréchet expansion about the free energy, it makes it difficult to quickly parse the meaning of an equation when one is looking upon a sea of Ψ s.

Eq. (2.6) (recall that $\eta(t)$ is also derived from $\Psi(t)$, see Chapter 3 and Eq. (3.22)),

$$\begin{split} E^{\text{pot}} &= \frac{1}{2} K_D\left(\mathbf{\hat{e}}, \theta\right) \int_0^t \int_0^t f_1\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{dI_1}{du} ds \, du + \frac{1}{2} K_{\infty}\left(\mathbf{\hat{e}}, \theta\right) I_1^2 \\ &+ G_D\left(\mathbf{\hat{e}}, \theta\right) \int_0^t \int_0^t f_2\left(t^* - s^*, t^* - u^*\right) \frac{d\mathbf{\hat{e}}}{ds} \vdots \frac{d\mathbf{\hat{e}}}{du} ds \, du + G_{\infty}\left(\mathbf{\hat{e}}, \theta\right) \mathbf{\hat{e}} : \mathbf{\hat{e}} \\ &- L_D\left(\mathbf{\hat{e}}, \theta\right) \int_0^t \int_0^t f_3\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\theta}{du} ds \, du + L_D\left(\mathbf{\hat{e}}, \theta\right) \left(\theta - \theta_{\text{sf}}\right) I_1 \\ &- L_D^{\text{ref}}\left(\theta_{\text{ref}} - \theta_{\text{sf}}\right) I_1, \text{ref} \\ &- \frac{C_D\left(\theta\right)}{2\theta_{\text{ref}}} \int_0^t f_4\left(t^* - s^*, t^* - u^*\right) \frac{d\theta}{ds} \frac{d\theta}{du} ds \, du + \frac{C_D\left(\theta\right)}{2\theta_{\text{ref}}} \left(\theta - \theta_{\text{ref}}\right)^2 \\ &+ \theta \left[L_D\left(\mathbf{\hat{e}}, \theta\right) \int_0^t f_3\left(t^* - s^*\right) \frac{dI_1}{ds} \, ds - L_D\left(\mathbf{\hat{e}}, \theta\right) I_1 + \frac{\theta_{\text{ref}}}{\theta} L_D^{\text{ref}}^{\text{ref}} I_1, \text{ref} \\ &+ \frac{C_D\left(\theta\right)}{\theta_{\text{ref}}} \int_0^t f_4\left(t^* - s^*\right) \frac{d\theta}{ds} \, ds - \frac{C_D\left(\theta\right)}{\theta_{\text{ref}}} \left(\theta - \theta_{\text{ref}}\right) \\ &- \frac{1}{2} K_D^{\theta} \int_0^t \int_0^t f_1\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du - \frac{1}{2} K_{\infty}^{\theta} I_1^2 \\ &- G_D^{\theta} \int_0^t \int_0^t f_2\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{dI_1}{du} \, ds \, du - \frac{1}{2} K_{\infty}^{\theta} I_1^2 \\ &- G_D^{\theta} \int_0^t \int_0^t f_3\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{dH}{ds} \, ds \, du - G_{\infty}^{\theta} \mathbf{\hat{e}} : \mathbf{\hat{e}} \\ &+ \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\theta}{du} \, ds \, du - G_{\infty}^{\theta} \mathbf{\hat{e}} : \mathbf{\hat{e}} \\ &+ \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\theta}{du} \, ds \, du - G_{\infty}^{\theta} \mathbf{\hat{e}} : \mathbf{\hat{e}} \\ &+ \frac{\partial L_D}{\partial \theta} \int_0^t \int_0^t f_3\left(t^* - s^*, t^* - u^*\right) \frac{dI_1}{ds} \frac{d\theta}{du} \, ds \, du - G_{\infty}^{\theta} \mathbf{\hat{e}} : \mathbf{\hat{e}} \\ &+ \frac{\partial L_D}{\partial \theta} \int_{\theta=\theta_{\text{ref}}}^t I_1, \text{ref} \left(\theta_{\text{ref}} - \theta_{\text{sf}}\right) \\ &+ \frac{C_D^{\theta}}{2\theta_{\text{ref}}} \int_0^t \int_0^t f_4\left(t^* - s^*, t^* - u^*\right) \frac{d\theta}{ds} \frac{d\theta}{du} \, ds \, du - \frac{\partial L_D}{\partial \theta} I_1\left(\theta - \theta_{\text{sf}}\right) \\ &+ \frac{\partial L_D}{\partial \theta} \int_{\theta=\theta_{\text{ref}}}^t I_1, \text{ref} \left(\theta_{\text{ref}} - \theta_{\text{sf}}\right) \\ &+ \frac{\partial L_D}{\partial \theta} \int_{\theta=\theta_{\text{ref}}}^t I_1, \text{ref} \left(\theta_{\text{ref}} - \theta_{\text{sf}}\right) \\ &+ \frac{\partial L_D}{\partial \theta} \int_{\theta=\theta_{\text{ref}}}^t I_1\left(\theta_{\text{ref}} - \theta_{\text{sf}}\right) \\ &+ \frac{\partial L_D}{$$

In PEC, $\theta_{ref} = \theta_{sf}$, but Spectacular allows them to be different. To maintain a shift factor of unity at θ_{ref} under stress-free, equilibrium conditions, E^{pot} must equal zero at θ_{ref} under stress-free, equilibrium conditions. To accommodate this, the constant orange and magenta terms in Eq. (B.1) were added.

Rather than writing every single term in E^{pot} , as has been done in Eq. (B.1), it is simpler to show how E^{pot} has been modified from $E = \Psi + \theta \eta$. In this case, converting X_{∞} terms to $-X_D$ terms is equivalent to subtracting X_g ,

$$E^{\text{pot}} = \Psi + \theta \eta$$

+ $L_g \left(\boldsymbol{\epsilon}, \theta \right) \left(\theta - \theta_{\text{sf}} \right) I_1 - L_D^{\text{ref}} \left(\theta_{\text{ref}} - \theta_{\text{sf}} \right) I_{1,\text{ref}} + \frac{C_g \left(\theta \right)}{2\theta_{\text{ref}}} \left(\theta - \theta_{\text{ref}} \right)^2$
- $\theta L_g \left(\boldsymbol{\epsilon}, \theta \right) I_1 + \theta_{\text{ref}} L_D^{\text{ref}} I_{1,\text{ref}} - \theta \frac{C_g \left(\theta \right)}{\theta_{\text{ref}}} \left(\theta - \theta_{\text{ref}} \right)$
- $\theta \frac{\partial L_g}{\partial \theta} I_1 \left(\theta - \theta_{\text{sf}} \right) + \theta_{\text{ref}} \left. \frac{\partial L_D}{\partial \theta} \right|_{\substack{\boldsymbol{\epsilon} = \mathbf{0} \\ \theta = \theta_{\text{ref}}}} I_{1,\text{ref}} \left(\theta_{\text{ref}} - \theta_{\text{sf}} \right) - \theta \frac{C_g^{\theta}}{2\theta_{\text{ref}}} \left(\theta - \theta_{\text{ref}} \right)^2.$ (B.2)

The constant terms added to keep the equilibrium E^{pot} equal to zero at θ_{ref} are also shown in Eq. (B.2).

B.2. Derivation of the simplified potential energy used in the Spectacular clock

In simplifying from PEC to SPEC, most of the terms in Eq. (B.1) were eliminated and integral prefactors were approximated to be constant by choosing their value at θ_{ref} and zero strain. In the simplified potential energy, only the blue and magenta terms in Eq. (B.1) were kept, giving the following expression for the simplified potential energy \tilde{E}^{pot} ,

$$\tilde{E}^{\text{pot}} = G_D^{\text{ref}} \int_0^t \int_0^t f_2 \left(t^* - s^*, t^* - u^* \right) \frac{d\boldsymbol{e}}{ds} : \frac{d\boldsymbol{e}}{du} \, ds \, du
+ L_D^{\text{ref}} \theta_{\text{ref}} \int_0^t f_3 \left(t^* - s^* \right) \frac{dI_1}{ds} \, ds - L_D^{\text{ref}} I_1 \theta_{\text{ref}} + L_D^{\text{ref}} I_{1,\text{ref}} \theta_{\text{ref}}
+ C_D^{\text{ref}} \int_0^t f_4 \left(t^* - s^* \right) \frac{d\theta}{ds} \, ds - C_D^{\text{ref}} \left(\theta - \theta_{\text{ref}} \right).$$
(B.3)

The rationale for the terms kept in Eq. (B.3) is described in Adolf et al. 2009 [7]. Briefly, first-order integral terms were kept along with their corresponding equilibrium terms and the second-order integral term involving the deviatoric strain was kept because yield cannot be predicted using only the first-order integrals. The equilibrium term corresponding to the second-order integral was **not** kept because $G_D^{\text{ref}} >> G_{\infty}^{\text{ref}}$.

For SPEC [7], the simplified potential energy was converted into a temperature-like quantity by dividing by $-C_D^{\text{ref}}$. In Spectacular, the simplified potential energy was converted into an absolute temperature-like quantity by dividing by $-C_D^{\text{ref}}$ and adding θ_{ref} ;

$$N = \frac{\tilde{E}^{\text{pot}}}{-C_D^{\text{ref}}} + \theta_{\text{ref}},$$
(B.4)

$$N = \frac{G_D^{\text{ref}}}{-C_D^{\text{ref}}} \int_0^t \int_0^t f_2 (t^* - s^*, t^* - u^*) \frac{d\mathbf{e}}{ds} : \frac{d\mathbf{e}}{du} \, ds \, du$$

$$+ \frac{L_D^{\text{ref}} \theta_{\text{ref}}}{C_D^{\text{ref}}} \left[I_1 - I_{1,\text{ref}} - \int_0^t f_3 (t^* - s^*) \frac{dI_1}{ds} \, ds \right]$$

$$+ \theta - \int_0^t f_4 (t^* - s^*) \frac{d\theta}{ds} \, ds.$$
(B.5)

Converting *N* into an absolute temperature was done to facilitate explorations of other shift factor models that depend on the absolute temperature, like the Arrhenius model.

Finally, Eq. (2.46) is recovered by changing the material parameter prefactors to free parameters,

$$N = \Theta - \int_0^t f_4 (t^* - s^*) \frac{d\Theta}{ds} ds + C_3 \left[I_1 - I_{1,ref} - \int_0^t f_3 (t^* - s^*) \frac{dI_1}{ds} ds \right] + C_4 \int_0^t \int_0^t f_2 (t^* - s^*, t^* - u^*) \frac{d\mathbf{e}}{ds} : \frac{d\mathbf{e}}{du} ds du.$$
(B.6)

This derivation shows that choosing V = 3, T = 4 in Eq. (2.46) are the only choices consistent with the simplification procedure in Adolf et al. 2009 [7]. Based on the simplification procedure, the parameters C_3 and C_4 should be

$$C_3 = \frac{L_D^{\text{ref}} \theta_{\text{ref}}}{C_D^{\text{ref}}}, \qquad \qquad C_4 = \frac{G_D^{\text{ref}}}{-C_D^{\text{ref}}}. \tag{B.7}$$

However, the simplifications from E^{pot} to N were so severe that Eq. (B.7) is not expected to hold true [7]. However, L_D^{ref} and C_D^{ref} are both negative, so C_3 should always be positive. Likewise, G_D^{ref} and $-C_D^{\text{ref}}$ are both positive, so C_4 should always be positive. Note, that C_3 and C_4 would both depend on the temperature and strain if no simplifications had been made when converting E^{pot} to N.

B.3. Method for comparing the Spectacular and PEC clocks

By subjecting E^{pot} to the same transformation used to go from \tilde{E}^{pot} to N, a non-simplified clock temperature N^{PEC} can be derived for comparing the Spectacular and PEC clocks,

$$N^{\text{PEC}} = \frac{E^{\text{pot}}}{-C_D^{\text{ref}}} + \theta_{\text{ref}}.$$
(B.8)

Now, N^{PEC} can be used as an argument in the Spectacular shift factor function, Eq. (2.43) to determine a hypothetical PEC shift factor,

$$\log a^{\text{PEC}} = \log a \left(N^{\text{PEC}} \right) = \begin{cases} -\frac{C_1 \left(N^{\text{PEC}} - \theta_{\text{ref}} \right)}{C_2 + N^{\text{PEC}} - \theta_{\text{ref}}}, & N^{\text{PEC}} \ge N_{\text{match}}, \\ A_1 + \frac{A_2}{N^{\text{PEC}}}, & N^{\text{PEC}} < N_{\text{match}}. \end{cases}$$
(B.9)

The quantities E^{pot} , N^{PEC} and $\log a^{\text{PEC}}$ have been added as state variables in Spectacular. In no way is $\log a^{\text{PEC}}$ used in Spectacular. It is only calculated after the Newton-Raphson loop for comparison to the converged $\log a$ using N. If, for a given thermo-mechanical history, $\log a \approx \log a^{\text{PEC}}$, then the simplifications used to derive N are justified, and there is no need to explore a clock using E^{pot} . On the other hand, if $\log a$ and $\log a^{\text{PEC}}$ are significantly different, then it is possible that the E^{pot} -based clock would enable more sophisticated physical aging predictions using a single model calibration; predictions that have so far been elusive using the N-based clock.

C. LEIBNIZ INTEGRAL RULE FOR DIFFERENTIATION UNDER THE INTEGRAL SIGN

The Leibniz rule for differentiation under the integral sign [34] is

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{A(t)}^{B(t)} g(t,s)\,\mathrm{d}s\right) = g\left(t,B(t)\right) \cdot \frac{\mathrm{d}B}{\mathrm{d}t} - g\left(t,A(t)\right) \cdot \frac{\mathrm{d}A}{\mathrm{d}t} + \int_{A(t)}^{B(t)} \frac{\partial}{\partial t}g(t,s)\,\mathrm{d}s. \tag{C.1}$$

This rule is useful for taking time-derivatives of the single and double hereditary convolution integrals that appear in Spectacular. Specifically, the following time-derivatives appear when deriving the stress and entropy from the Helmholtz free energy (Chapter 3) or the establishing numerical implementation of the model (Chapter 4):

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_0^t f_r \left(t^* - s^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \tag{C.2}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_0^t \int_0^t f_r \left(t^* - s^*, t^* - u^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \frac{\mathrm{d}\phi}{\mathrm{d}u} \mathrm{d}s \,\mathrm{d}u \tag{C.3}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_0^t \exp\left(-\frac{t^* - s^*}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \mathrm{d}s = \frac{\mathrm{d}}{\mathrm{d}t} J_{rp}^{\xi}.$$
 (C.4)

The symbol f_r represents any of the relaxation functions and τ_{rp} is the *p*-th Prony term in relaxation function *r*. Generic state variable histories are represented by ξ and ϕ , which in Spectacular could be histories of the volume strain, deviatoric strain tensor, or temperature; $\xi, \phi \in \{I_1, \boldsymbol{e}, \theta\}$. The symbol J_{rp}^{ξ} is used as shorthand for a hereditary convolution integral on the *p*-th Prony term of the relaxation function *r* and the state variable history ξ .

When applying the Leibniz rule to any of Eqs. (C.2) to (C.4),

$$A(t) = 0, \qquad \qquad \frac{\mathrm{d}A}{\mathrm{d}t} = 0 \qquad (C.5)$$

. .

$$B(t) = t, \qquad \qquad \frac{\mathrm{d}B}{\mathrm{d}t} = 1. \tag{C.6}$$

Under these assumptions, the Liebniz rule simplifies to

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_0^t g(t,s)\,\mathrm{d}s\right) = g\left(t,t\right) + \int_0^t \frac{\partial}{\partial t}g(t,s)\,\mathrm{d}s. \tag{C.7}$$

In this appendix, expressions for Eqs. (C.2) to (C.4) are derived using Eq. (C.7).

C.1. Time-derivative of a single hereditary integral

To evaluate Eq. (C.2), set

$$g(t,s) = f_r \left(t^* - s^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s}.$$
 (C.8)

To evaluate the time-derivative of a single hereditary integral, combine Eqs. (C.7) and (C.8) and simplify;

$$\begin{split} \frac{\mathrm{d}}{\mathrm{d}t} & \int_0^t f_r \left(t^* - s^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \, \mathrm{d}s = g\left(t, t\right) + \int_0^t \frac{\partial}{\partial t} g(t, s) \, \mathrm{d}s \\ &= f_r \left(t^* - t^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}t} + \int_0^t \frac{\partial f_r \left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} \, \mathrm{d}s \\ &= \dot{\xi} + \int_0^t \frac{\partial f_r \left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} \, \mathrm{d}s. \end{split}$$

Therefore, the time-derivative of the single hereditary integral is

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_0^t f_r \left(t^* - s^*\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s = \dot{\xi} + \int_0^t \frac{\partial f_r \left(t^* - s^*\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s. \tag{C.9}$$

C.2. Time-derivative of a double hereditary integral

To evaluate Eq. (C.3), set

$$g(t,s,u) = \int_0^t f_r \left(t^* - s^*, t^* - u^*\right) \frac{d\xi}{ds} \frac{d\phi}{du} du.$$
 (C.10)

To evaluate the time-derivative of a double hereditary integral, combine Eqs. (C.7) and (C.10) and simplify;

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \int_{0}^{t} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \frac{\mathrm{d}\phi}{\mathrm{d}u} \mathrm{d}s \,\mathrm{d}u &= g\left(t, t, u\right) + \int_{0}^{t} \left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_{s} g(t, s, u) \,\mathrm{d}s \\ &= \int_{0}^{t} f_{r} \left(t^{*} - t^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\xi}{\mathrm{d}t} \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u + \int_{0}^{t} \left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_{s} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u \\ &= \frac{\mathrm{d}\xi}{\mathrm{d}t} \int_{0}^{t} f_{r} \left(0, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u + \int_{0}^{t} \left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_{s} \left\{\int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u \right\} \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \\ &= \dot{\xi} \int_{0}^{t} f_{r} \left(t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u + \int_{0}^{t} \left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_{s} \left\{\int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u \right\} \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \end{aligned}$$

To evaluate the term in curly brackets ($\{\}$), recursively use the Liebniz rule, but keep *s* constant, since its variation was already accounted for in the first application of the Liebniz rule. For the second application of the Leibniz rule,

$$\hat{g}(t,s,u) = f_r (t^* - s^*, t^* - u^*) \frac{\mathrm{d}\phi}{\mathrm{d}u}.$$
 (C.11)

Working through the combination of Eqs. (C.7) and (C.11) gives

$$\begin{pmatrix} \frac{\mathrm{d}}{\mathrm{d}t} \end{pmatrix}_{s} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \mathrm{d}u = \hat{g}(t, s, t) + \int_{0}^{t} \frac{\partial}{\partial t} \hat{g}(t, s, u) \mathrm{d}u$$

$$= f_{r} \left(t^{*} - s^{*}, t^{*} - t^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}t} + \int_{0}^{t} \frac{\partial}{\partial t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \mathrm{d}u$$

$$= \dot{\phi} f_{r} \left(t^{*} - s^{*}\right) + \int_{0}^{t} \frac{\partial}{\partial t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \mathrm{d}u.$$

Use this result to continue simplifying:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} & \int_{0}^{t} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}s \,\mathrm{d}u \\ &= \dot{\xi} \int_{0}^{t} f_{r} \left(t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u + \int_{0}^{t} \left\{ \dot{\phi} f_{r} \left(t^{*} - s^{*}\right) + \int_{0}^{t} \frac{\partial}{\partial t} f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u \right\} \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \\ &= \dot{\xi} \int_{0}^{t} f_{r} \left(t^{*} - u^{*}\right) \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}u + \dot{\phi} \int_{0}^{t} f_{r} \left(t^{*} - s^{*}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s + \int_{0}^{t} \int_{0}^{t} \frac{\partial f_{r} \left(t^{*} - s^{*}, t^{*} - u^{*}\right)}{\partial t} \frac{\mathrm{d}\xi}{\mathrm{d}s} \frac{\mathrm{d}\phi}{\mathrm{d}u} \,\mathrm{d}s \,\mathrm{d}u. \end{aligned}$$

Finally, the time-derivative of the double hereditary integral is

$$\frac{d}{dt} \int_{0}^{t} \int_{0}^{t} f_{r} (t^{*} - s^{*}, t^{*} - u^{*}) \frac{d\xi}{ds} \frac{d\phi}{du} ds du$$

$$= \dot{\xi} \int_{0}^{t} f_{r} (t^{*} - s^{*}) \frac{d\phi}{ds} ds + \dot{\phi} \int_{0}^{t} f_{r} (t^{*} - s^{*}) \frac{d\xi}{ds} ds$$

$$+ \int_{0}^{t} \int_{0}^{t} \frac{\partial f_{r} (t^{*} - s^{*}, t^{*} - u^{*})}{\partial t} \frac{d\xi}{ds} \frac{d\phi}{du} ds du.$$
(C.12)

C.3. Time derivative of a Prony integral

For Eq. (C.4), start with the result for the single hereditary integral in Eq. (C.9), but plug in a single Prony term relaxation function for f_r ;

$$f_r(t^* - s^*) = \exp\left(-\frac{t^* - s^*}{\tau_{rp}}\right).$$
 (C.13)

Combining Eqs. (C.9) and (C.13) gives

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \int_{0}^{t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s &= \dot{\xi} + \int_{0}^{t} \frac{\partial}{\partial t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \\ &= \dot{\xi} + \int_{0}^{t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \left[\frac{\partial}{\partial t} \left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right)\right] \,\mathrm{d}s \\ &= \dot{\xi} + \int_{0}^{t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \left[\frac{\mathrm{d}t^{*}}{\mathrm{d}t} \frac{\partial}{\partial t^{*}} \left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right)\right] \,\mathrm{d}s \\ &= \dot{\xi} + \int_{0}^{t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \left[-\frac{1}{a\tau_{rp}}\right] \,\mathrm{d}s \\ &= \dot{\xi} - \left(\frac{1}{a\tau_{rp}}\right) \int_{0}^{t} \exp\left(-\frac{t^{*}-s^{*}}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s \\ &= \dot{\xi} - \left(\frac{1}{a\tau_{rp}}\right) J_{rp}^{\xi}. \end{aligned}$$

Therefore, the time-derivative of a single Prony term evaluates to

$$\frac{\mathrm{d}}{\mathrm{d}t}J_{rp}^{\xi} = \dot{\xi} - \left(\frac{1}{a\tau_{rp}}\right)J_{rp}^{\xi}.$$
(C.14)

Recall that

$$J_{rp}^{\xi} \coloneqq \int_0^t \exp\left(-\frac{t^*-s^*}{\tau_{rp}}\right) \frac{\mathrm{d}\xi}{\mathrm{d}s} \,\mathrm{d}s.$$

D. CALIBRATION FOR 828/DEA USED TO SIMULATE YIELD STRESS EVOLUTION AFTER ISOTHERMAL AGING

These parameters were used to predict yield stress evolution under isothermal aging, see Fig. 5-3. The calibration was taken from Table 5-5 in Ref. [1], but values for E_a/R and θ_{match} were chosen to get the model to reach an equilibrium yield stress at the same timescale observed in experiments, approximately 1000 h.

```
# Material: 828/DEA
# Calibration: SAND2021-11193, Table 5-5 (DSC-focused)
# Table 5-5 only lists parameters that changed from the baseline 828dea
# calibration (baseline followed a traditional SPEC calibration approach,
# see 2009_adolf_a). The baseline 828dea parameters are listed in Table 5-1.
# Some parameters were not re-calibrated in sand2021-11193, so are taken from
\# the literature. These parameters are marked here (and in Table 5-1).
# REFS
# 2009_adolf_a: A simplified potential energy clock model for glassy polymers
# 2004_adolf_a: Extensive validation of a thermodynamically consistent,
# nonlinear viscoelastic model for glassy polymers.
# NOTE: Set stress free-temperature based on application
begin property specification for material 828dea
       density = 1176 # kg/m^3 (2004_adolf_a, Table 4)
       thermal log strain function = sierra_constant_function_zero
             tin parameters for model spectacular

bulk modulus = 4.9E9 # Pa (2009_adolf_a, Table 3)

shear modulus = 0.9E9 # Pa (2009_adolf_a, Table 3)

bulk glassy 0 = 4.9E9 # Pa (2009_adolf_a, Table 3)

bulk glassy 1 = -12.0E6 # Pa/K (2009_adolf_a, Table 3)

bulk rubbery 0 = 3.2E9 # Pa (2009_adolf_a, Table 3)

bulk rubbery 1 = -12.0E6 # Pa/K (2009_adolf_a, Table 3)

shear glassy 0 = 0.9E9 # Pa (2009_adolf_a, Table 3)

shear glassy 1 = -4.2E6 # Pa/K (2009_adolf_a, Table 3)

shear rubbery 0 = 4.5E6 # Pa (2009_adolf_a, Table 3)

shear rubbery 1 = 0 # Pa/K (2009_adolf_a, Table 3)

shear rubbery 1 = 0 # Pa/K (2009_adolf_a, Table 3)

shear rubbery 1 = 0 # Pa/K (2009_adolf_a, Table 3)

volcte glassy 1 = -4.2E6 # Pa (2009_adolf_a, Table 3)

shear rubbery 1 = 0 # Fa/K (2009_adolf_a, Table 3)

volcte glassy 0 = 220E-6 # K^-1

volcte rubbery 1 = 0 # Fa/K (2009_adolf_a, Table 3)

heat capacity glassy 0 = 1172000 # J/(m^3*K)

heat capacity glassy 1 = 2160 # J/(m^3*K)

heat capacity rubbery 0 = 1381000 # J/(m^3*K)

heat capacity rubbery 1 = 690 # J/(m^3*K^2)
       begin parameters for model spectacular
              heat capacity rubbery 1 = 690
                                                                                       # J/(m^3*K^2)
               reference temperature = 348.15
                                                                                       # K
```

```
wlf cl
                   = 12.6
                                  # None
                   = 40.1
wlf c2
                                  # K
clock cl
                    = 0
                                  # None
                    = 0
clock c2
                                  # K
                    = 1000
clock c3
                                  # K
                                                 (2009_adolf_a, Table 3)
                    = 9900
clock c4
                                   # K
stress free temperature = {stress_free_temperature} # K
# === NEW PARAMETERS ADDED AFTER SAND2021-11193 ===
clock c0
           = 1
                           # None
                   = 3
N_THERMAL_FUNCTION
N_VOLUME_FUNCTION
                    = 1
TMATCH_WLF_ARH
                   = 344.15
                    = 15000
EACT ON R
                                  # K
# ===
#RELAX TIMEi terms have units of s
#Fi terms are unitless
# Spectrum ID 1 (volumetric)
# Prony series fit to KWW parameters:
# logkwwtau_3 = 1.612368827, kwwbeta_3 = 0.2565190905
\# kwwtau 3 = 40.96083742
# Spectrum ID = 1
   RELAX_TIME1 = 2.71804127e-10 8.91933354e-10 2.92690592e-09 9.60472913e
       -09 3.15182053e-08 1.03427931e-07 3.39401844e-07 1.11375728e-06
         3.65482776e-06 1.19934264e-05 3.93567866e-05 1.29150470e-04
       4.23811121e-04 1.39074884e-03 4.56378384e-03 1.49761929e-02
       4.91448239e-02 1.61270206e-01 5.29212995e-01 1.73662824e+00
       5.69879739e+00 1.87007737e+01 6.13671472e+01 2.01378125e+02
       6.60828327e+02 2.16852788e+03 7.11608896e+03 2.33516583e+04
       7.66291636e+04
   F1 = 4.53538570e-04 4.47517764e-04 5.96311960e-04 8.51522565e-04
       1.11972073e-03 1.53917871e-03 2.07119589e-03 2.81153266e-03
       3.79826868e-03 5.13524205e-03 6.92818409e-03 9.33292425e-03
       1.25392707e-02 1.67902812e-02 2.23776424e-02 2.96328821e-02
       3.88977547e-02 5.04377753e-02 6.43099029e-02 8.00704119e-02
       9.64399649e-02 1.10750090e-01 1.18853727e-01 1.15487239e-01
       9.72100198e-02 6.59384129e-02 3.27717625e-02 9.87267126e-03
       1.69787997e-03
# Spectrum ID 2 (shear)
# Prony series fit to KWW parameters:
# logkwwtau_2 = 0.09691, kwwbeta_2 = 0.23
\# kwwtau 2 = 1.25
# Spectrum ID = 2
   RELAX TIME2 =
                4.26536725e-13 1.60522752e-12 6.04111025e-12 2.27351031e
       -11 8.55612445e-11 3.22001028e-10 1.21181807e-09 4.56055387e-09
         1.71631800e-08 6.45918795e-08 2.43084959e-07 9.14825482e-07
       3.44285252e-06 1.29568248e-05 4.87616902e-05 1.83509654e-04
       6.90619890e-04 2.59907761e-03 9.78136384e-03 3.68111665e-02
       1.38535075e-01 5.21362645e-01 1.96209521e+00 7.38414545e+00
       2.77894792e+01 1.04582874e+02 3.93586995e+02 1.48122456e+03
```

```
5.57443777e+03
   F2 = 5.12254889e-04 3.88190023e-04 6.72038171e-04 8.37774138e-04
      1.17447444e-03 1.56963583e-03 2.13750996e-03 2.88628165e-03
      3.90693817e-03 5.27581435e-03 7.11793124e-03 9.58208471e-03
      1.28660633e-02 1.72116024e-02 2.29110557e-02 3.02896794e-02
      3.96734709e-02 5.12985678e-02 6.51671709e-02 8.07637657e-02
      9.67191410e-02 1.10330692e-01 1.17537228e-01 1.13432247e-01
      9.50885713e-02 6.46967591e-02 3.27688423e-02 1.03280657e-02
      2.00345285e-03
# Spectrum ID 3 (thermal-volumetric)
# Prony series fit to KWW parameters:
# logkwwtau 3 = 2.949326293, kwwbeta 3 = 0.2192070888
\# kwwtau_3 = 889.8694412
# Spectrum ID = 3
   RELAX TIME3 = 7.38835954e-11 2.96802486e-10 1.19230412e-09 4.78968065e
      -09 1.92409305e-08 7.72939643e-08 3.10502495e-07 1.24733930e-06
         5.01076596e-06 2.01290663e-05 8.08617513e-05 3.24834879e-04
      1.30491483e-03 5.24205628e-03 2.10581974e-02 8.45942226e-02
      3.39828827e-01 1.36514797e+00 5.48402265e+00 2.20302158e+01
      8.84989798e+01 3.55514875e+02 1.42816139e+03 5.73715787e+03
      2.30471014e+04 9.25839755e+04 3.71924971e+05 1.49408343e+06
      6.00197748e+06
   F3 = 5.30681676e-04 3.75188923e-04 6.91493931e-04 8.40255308e-04
      1.19093541e-03 1.58508713e-03 2.16177072e-03 2.91724436e-03
      3.94932932e-03 5.33211426e-03 7.19302015e-03 9.68121661e-03
      1.29957746e-02 1.73790259e-02 2.31229622e-02 3.05507512e-02
      3.99820394e-02 5.16416058e-02 6.55102494e-02 8.10447982e-02
      9.68409736e-02 1.10183832e-01 1.17042559e-01 1.12647771e-01
      9.42579923e-02 6.41817675e-02 3.27126208e-02
                                                      1.04778267e-02
      2.12001456e-03
# Spectrum ID 4 (thermal)
# Prony series fit to KWW parameters:
\# logkwwtau 4 = 2.949326293, kwwbeta 4 = 0.2192070888
\# kwwtau 4 = 889.8694412
# Spectrum ID = 4
   RELAX_TIME4 = 7.38835954e-11 2.96802486e-10 1.19230412e-09
                                                                4.78968065e
      -09 1.92409305e-08 7.72939643e-08 3.10502495e-07 1.24733930e-06
         5.01076596e-06 2.01290663e-05 8.08617513e-05 3.24834879e-04
      1.30491483e-03 5.24205628e-03 2.10581974e-02 8.45942226e-02
      3.39828827e-01 1.36514797e+00 5.48402265e+00 2.20302158e+01
      8.84989798e+01 3.55514875e+02 1.42816139e+03 5.73715787e+03
      2.30471014e+04 9.25839755e+04 3.71924971e+05 1.49408343e+06
      6.00197748e+06
   F4 = 5.30681676e-04 3.75188923e-04 6.91493931e-04
                                                         8.40255308e-04
      1.19093541e-03 1.58508713e-03 2.16177072e-03 2.91724436e-03
      3.94932932e-03 5.33211426e-03 7.19302015e-03 9.68121661e-03
      1.29957746e-02 1.73790259e-02 2.31229622e-02 3.05507512e-02
      3.99820394e-02 5.16416058e-02 6.55102494e-02 8.10447982e-02
      9.68409736e-02 1.10183832e-01 1.17042559e-01 1.12647771e-01
      9.42579923e-02 6.41817675e-02 3.27126208e-02 1.04778267e-02
      2.12001456e-03
```

end parameters for model spectacular

end property specification for material 828dea

E. CALIBRATION FOR 828/DEA USED TO SIMULATE CREEP

These parameters were used to simulate creep, see Figs. 5-4 and 5-5. The parameters were generated using data on 828/DEA from Ref. [1], but the parameters are different from the calibrations in Ref. [1] due to the use of the new FY23 model features.

```
# Material: 828/DEA
#
# Calibration: FY23Q4-ARH-SLOWCOOLDSCF4
#
# Calibrated by: Ken Cundiff (kcundif@sandia.gov), FY23
begin material 828_dea
    density = 1176 \# kg/m^3 (2004 Adolf et al., Table 4)
    thermal log strain function = sierra_constant_function_zero
    begin parameters for model spectacular
        bulk modulus = 4.9E9
                                                 # Pa
                                                                    (2009 Adolf et al., Table 3)
        shear modulus
                                 = 0.800E9
                                                 # Pa
        ### Bulk modulus ###
                                bulk glassy O
                                                                    (2009 Adolf et al., Table 3)
                                                                  (2009 Adolf et al., Table 3)
        bulk glassy 1
                                                                   (2009 Adolf et al., Table 3)
        bulk rubbery 0
                                  bulk rubbery 1
                                                                    (2009 Adolf et al., Table 3)
        ### Shear modulus ###
        shear glassy 0
                                 = 0.800E9
                                                   # Pa
        shear glassy 0= 0.000E9# Fashear glassy 1= -3.553E6# Pa/Kshear glassy 2= {shear_glassy_I1} # Pashear glassy 3= {shear_glassy_I2} # Pashear glassy 4= {shear_glassy_I3} # Pashear rubbery 0= 6.000E6# Pa/Kshear rubbery 1= 33.399E3# Pa/K
        shear rubbery 2
                               = {shear_rubbery_I1} # Pa
        shear rubbery 3
                               = {shear_rubbery_I2} # Pa
        shear rubbery 4
                                 = {shear_rubbery_I3} # Pa
        ### CTE ###
        volcte glassy 0
                                 = 236E-6
                                                   # K^−1
                                 = 0.0E-6
        volcte glassy 1
                                                   # K^-2
        volcte rubbery 0
                                 = 546E-6
                                                  # K^−1
        volcte rubbery 1
                                 = 0.8E-6
                                                   # K^−2
        ### Heat capacity (constant volume) ###
        heat capacity glassy 0 = 1180000 # J/(m^3*K)
        heat capacity glassy 1 = 200
                                                 # J/(m^3*K^2)
        heat capacity rubbery 0 = 1360000# J/(m^3*K)heat capacity rubbery 1 = -500# J/(m^3*K)
                                                 # J/(m^3*K^2)
        ### Clock parameters ###
```

```
reference temperature = 348.15 # K
                                           (75C)
stress free temperature = {stress_free_temperature} # K
wlf cl
                    = 12.6 # None
wlf c2
                     = 40.1
                                    # K
                   = 344.15
tmatch wlf arh
                                   # K
                                            (71C)
                     = 137000
eact on r
                                    # K
### N Definition (aka clock temperature or potential energy, depending on how you
   want to look at it)
n thermal function
                    = 4
                                  # relaxation function index
n volume function
                     = 3
                                  # relaxation function index
                     = 1000
clock c3
                                  # K
                                            (2009 Adolf et al., Table 3)
clock c4
                     = 7500
                                    # K
### Not specified ###
#clock c0
                     = 1.0
                                # None (Default)
#clock cl
                    = 0
                                  # None ("wlf c1" is defined instead)
                    = 0
#clock c2
                                  # K ("wlf c2" is defined instead)
#nmatch wlf arh
                     = 0
                                  # K ("tmatch wlf arh" is defined instead)
                     = 0
                                  # K ("eact on r" is defined instead)
#clock arh2
#RELAX TIMEi terms have units of s
#Fi terms are unitless
# Spectrum ID 1 (volumetric)
# Prony series fit to KWW parameters:
# logkwwtau_1 = 2.314342201, kwwbeta_1 = 0.3088857304
\# kwwtau 1 = 206.225422 s
# Spectrum ID = 1
##KWW Relaxation Function with
##KWW_tau = 2.062254e+02, KWW_beta = 3.088857e-01
##and 28 prony terms in use
##Prony L2 Projection Error = 1.885753e-04
##
   RELAX TIME1 = 1.07473113e-07 7.73512869e-07 2.07515911e-06 5.56717996e
       -06
           1.49354777e-05 4.00684901e-05 1.07494646e-04 2.88383689e-04
          7.73667853e-04 2.07557490e-03 5.56829543e-03 1.49384703e-02
       4.00765184e-02 1.07516184e-01 2.88441471e-01 7.73822869e-01
       2.07599077e+00 5.56941111e+00 1.49414634e+01 4.00845483e+01
       1.07537727e+02 2.88499265e+02 7.73977916e+02 2.07640673e+03
                     1.49444571e+04 4.00925798e+04 1.07559274e+05
       5.57052703e+03
   F1 = 5.08481728e-04 1.25902139e-03 1.08761548e-04 1.58934102e-03
       1.07799727e-03 2.19398822e-03 2.48961773e-03 3.67959536e-03
       4.77618675e-03 6.57793830e-03 8.78901973e-03 1.18789960e-02
       1.59053450e-02 2.12779681e-02 2.82658857e-02 3.72918932e-02
       4.86553987e-02 6.25482131e-02 7.86780574e-02 9.59640051e-02
       1.11831065e-01 1.21908367e-01 1.20136742e-01 1.01768903e-01
       6.82355711e-02 3.21365464e-02 8.58427464e-03 1.07547603e-03
# Spectrum ID 2 (shear)
##KWW Relaxation Function with
##KWW tau = 1.250000e+00, KWW beta = 2.300000e-01
##and 29 prony terms in use
##Prony L2 Projection Error = 4.168628e-04
```

```
##
```

```
RELAX TIME2 = 4.26536725e-13 1.60522752e-12 6.04111025e-12 2.27351031e
      -11 8.55612445e-11 3.22001028e-10 1.21181807e-09 4.56055387e-09
         1.71631800e-08 6.45918795e-08 2.43084959e-07 9.14825482e-07
       3.44285252e-06 1.29568248e-05 4.87616902e-05 1.83509654e-04
       6.90619890e-04 2.59907761e-03 9.78136384e-03 3.68111665e-02
       1.38535075e-01 5.21362645e-01 1.96209521e+00 7.38414545e+00
       2.77894792e+01 1.04582874e+02 3.93586995e+02 1.48122456e+03
      5.57443777e+03
   F2 = 5.12254889e-04 3.88190023e-04 6.72038171e-04 8.37774138e-04
      1.17447444e-03 1.56963583e-03 2.13750996e-03 2.88628165e-03
      3.90693817e-03 5.27581435e-03 7.11793124e-03 9.58208471e-03
      1.28660633e-02 1.72116024e-02 2.29110557e-02 3.02896794e-02
      3.96734709e-02 5.12985678e-02 6.51671709e-02 8.07637657e-02
       9.67191410e-02 1.10330692e-01
                                       1.17537228e-01 1.13432247e-01
      9.50885713e-02 6.46967591e-02 3.27688423e-02 1.03280657e-02
      2.00345285e-03
# Spectrum ID 3 (thermal-volumetric)
# Prony series fit to KWW parameters:
# logkwwtau_3 = 2.314342201, kwwbeta_3 = 0.3088857304
\# kwwtau 3 = 206.225422 s
# Spectrum ID = 3
##KWW Relaxation Function with
##KWW_tau = 2.062254e+02, KWW_beta = 3.088857e-01
##and 28 prony terms in use
##Prony L2 Projection Error = 1.885753e-04
##
   RELAX_TIME3 = 1.07473113e-07 7.73512869e-07 2.07515911e-06 5.56717996e
      -06 1.49354777e-05 4.00684901e-05 1.07494646e-04 2.88383689e-04
         7.73667853e-04 2.07557490e-03 5.56829543e-03 1.49384703e-02
       4.00765184e-02 1.07516184e-01 2.88441471e-01 7.73822869e-01
       2.07599077e+00 5.56941111e+00 1.49414634e+01 4.00845483e+01
      1.07537727e+02 2.88499265e+02 7.73977916e+02 2.07640673e+03
      5.57052703e+03 1.49444571e+04 4.00925798e+04 1.07559274e+05
   F3 = 5.08481728e-04 1.25902139e-03 1.08761548e-04 1.58934102e-03
      1.07799727e-03 2.19398822e-03 2.48961773e-03 3.67959536e-03
       4.77618675e-03 6.57793830e-03 8.78901973e-03 1.18789960e-02
      1.59053450e-02 2.12779681e-02 2.82658857e-02 3.72918932e-02
      4.86553987e-02 6.25482131e-02 7.86780574e-02 9.59640051e-02
      1.11831065e-01 1.21908367e-01 1.20136742e-01 1.01768903e-01
       6.82355711e-02 3.21365464e-02 8.58427464e-03 1.07547603e-03
# Spectrum ID 4 (thermal)
# Prony series fit to KWW parameters:
# logkwwtau_4 = 2.516771986, kwwbeta_4 = 0.2304083554
\# kwwtau 4 = 328.679022 s
# Spectrum ID = 4
##KWW Relaxation Function with
\#\#KWW tau = 3.286790e+02, KWW beta = 2.304084e-01
##and 29 pronv terms in use
##Prony L2 Projection Error = 4.123126e-04
##
```

RELAX TIME4 = 1.18008619e-10 4.43071472e-10 1.66354229e-09 6.24588386e -09 2.34506002e-08 8.80468902e-08 3.30578100e-07 1.24117820e-06 4.66008884e-06 1.74966238e-05 6.56922766e-05 2.46646167e-04 9.26049986e-04 3.47691832e-03 1.30543288e-02 4.90133746e-02 1.84024083e-01 6.90931068e-01 2.59414818e+00 9.73990763e+00 3.65691526e+01 1.37301397e+02 5.15507530e+02 1.93550845e+03 7.26699950e+03 2.72844490e+04 1.02441339e+05 3.84623048e+05 1.44409367e+06 F4 = 5.11499762e-04 3.88794968e-04 6.71191926e-04 8.37754519e-04 1.17379887e-03 1.56907635e-03 2.13656751e-03 2.88511187e-03 3.90531621e-03 5.27367189e-03 7.11506702e-03 9.57830728e-03 1.28611186e-02 1.72052214e-02 2.29029795e-02 3.02797311e-02 3.96617162e-02 5.12855077e-02 6.51541273e-02 8.07531226e-02 9.67146276e-02 1.10336516e-01 1.17556402e-01 1.13462500e-01 9.51203606e-02 6.47161468e-02 3.27703676e-02 1.03220048e-02 1.99893533e-03

end parameters for model spectacular

end material 828_dea

DISTRIBUTION

Email—Internal

Name	Org.	Sandia Email Address
Michael Buche	01558	mrbuche@sandia.gov
Edwin Chiu	01558	echiu@sandia.gov
Ken Cundiff	01558	kcundif@sandia.gov
Brenton Elisberg	01556	belisbe@sandia.gov
Scott Grutzik	01558	sjgrutz@sandia.gov
Jamie Kropka	01853	jmkropk@sandia.gov
Brian Lester	01558	btleste@sandia.gov
Kevin Long	01558	knlong@sandia.gov
Stacy Nelson	01558	smnelso@sandia.gov
Jonel Ortiz	01556	jonorti@sandia.gov
Kendall Pierson	01542	khpiers@sandia.gov
Alyssa Skulborstad	01558	ajskulb@sandia.gov
Technical Library	1911	sanddocs@sandia.gov

Email—External

Name	Company Email Address	Company Name
Brandon Talamini	talamini1@llnl.gov	Lawrence Livermore National Laboratory



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.