J. Mech. Phys. Solids 206 (2026) 106372

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Finite strain thermoelasticity and the Third Law of thermodynamics

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ARTICLE INFO

Keywords:
Third Law of thermodynamics
Finite strains
Thermoelasticity
Specific heat coefficient
Polyconvexity
Free energy potential

ABSTRACT

This paper shows that commonly used large strain thermoelastic models in which the specific heat coefficient is constant or, at most, changes with temperature, are incompatible with the Third Law of thermodynamics, namely, that "*entropy should be zero at the Kelvin state, that is, absolute zero temperature*". In particular, it will be shown that the Third Law implies that the specific heat coefficient must vary with deformation for the coupling between mechanical and thermal effects to take place. In line with this result, a simple analytical constitutive model consistent with the Third Law will be proposed. The model will be based on a multiplicative decomposition of the specific heat into a deformation dependent part and a temperature dependent component. The resulting thermoelastic model complies with the Third Law and, in addition, the necessary convexity conditions that ensure the existence of real wave speeds. It can replicate existing entropic elasticity models for rubber, describe melting and softening behaviour, and converge to the classical relationships for linear thermoelasticity in the small strain regime.

1. Introduction

The accurate modelling of materials undergoing large strain quasi-static and transient dynamics requires a comprehensive treatment of thermal effects (Callen, 1985; Gurtin et al., 2009; Bonet et al., 2021a; Holzapfel, 2000). These effects can significantly influence the stress state during complex, rapidly evolving deformation patterns. In the fields of thermo-elasticity and thermo-inelasticity (Simo and Hughes, 1998), a substantial body of work has been developed to address such couplings (Bonet et al., 2021a; Holzapfel, 2000; Govindjee and Carlson, 2024). While most classical formulations use the deformation gradient $\boldsymbol{F}$ and temperature θ as the primary thermal variables (i.e. $\{\boldsymbol{F},\theta\}$), alternative formulations using entropy ζ (i.e. $\{\boldsymbol{F},\zeta\}$) or even internal energy $\mathcal{E}$ (i.e. $\{\boldsymbol{F},\mathcal{E}\}$) are also viable (Bonet et al., 2021a). Traditionally, thermal effects are incorporated via an additive decomposition of the free energy density split in mechanical, thermal and coupled effects (Chadwick, 1974), or via a multiplicative decomposition of the deformation gradient (Lu and Pister, 1975) into purely thermal and deformation driven components. Recently, Govindjee and Carlson (2024) has shown the equivalence of both approaches under certain conditions.

Historically, many thermoelastic models have treated the specific heat coefficient (at constant deformation) as a constant, a simplification that holds for moderate temperature variations and small to moderate strains, and naturally facilitates the demonstration of stability (Bonet et al., 2021b). However, experimental investigations, particularly in polymeric and elastomeric materials (Treloar, 1975), have demonstrated a notable dependence of specific heat on the state of deformation (Nieto Simavilla

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https://doi.org/10.1016/j.jmps.2025.106372
Received 30 June 2025; Received in revised form 20 August 2025; Accepted 18 September 2025

et al., 2018). Although several researchers (Reese and Govindjee, 1998) have proposed temperature- and deformation-dependent specific heats to model materials operating beyond conventional performance envelopes, such generalisations must be approached with caution. In particular, inappropriate choices of the specific heat function can result in free energy formulations that violate thermodynamic stability, leading to numerical instabilities and unphysical behaviour under extreme conditions, ultimately causing the breakdown of the computational simulation.

Assuming constant specific heat (or even specific heat that only depends upon temperature) inherently imposes a linear dependence of stress on temperature, a limitation that becomes critical in applications involving significant thermal excursions (in both low and high temperature ranges) (Kittel, 2005). To capture realistic material responses under such conditions, including phenomena such as thermal softening and phase transitions, it is essential to incorporate a temperature- and deformation-dependent specific heat. This is particularly vital for modelling high-temperature behaviour where melting and large-scale thermal degradation may occur. Consequently, the adoption of variable specific heat not only enhances model fidelity but is a necessary condition for predictive accuracy in non-linear thermoelastic and thermo-inelastic formulations.

Advanced constitutive modelling frameworks must satisfy the laws of thermodynamics to ensure physical realism and mathematical robustness. While the First and Second Laws (Coleman and Noll, 1963) — governing energy conservation and the non-negativity of entropy production — are routinely enforced in contemporary thermo-mechanical models (commonly referred to as *thermodynamically consistent models*), the Third Law is often neglected. The Third Law, also known as the *Nernst postulate*, asserts that for systems with non-degenerate ground states, *"the entropy of a system must approach zero as the temperature approaches absolute zero"* (Callen, 1985; Ericksen, 1998). This requirement imposes significant constraints on the form of the free energy and the thermal constitutive relations. In particular, any model that employs constant specific heat or linear stress–temperature dependence inherently violates this condition. As will be demonstrated in this work, strict adherence to the Third Law *(i)* necessitates the use of deformation- and temperature-dependent specific heat, *(ii)* results in a fundamentally nonlinear stress–temperature coupling, and *(iii)* provides a natural thermodynamic pathway for describing melting and softening phenomena. Such adherence not only ensures consistency in extreme thermal regimes but also enhances the predictive capabilities of thermoelastic and thermo-inelastic models under large thermal excursions and phase transformation scenarios.

Furthermore, the formulation proposed herein is grounded in a polyconvex thermodynamic potential framework, a choice motivated by the need for both mathematical well-posedness and thermodynamic consistency across a wide range of deformations and temperatures (Ball, 1976; Šilhavý, 1997). Polyconvexity — a condition stronger than rank-one convexity — ensures the existence of minimisers for the associated variational problems and plays a central role in guaranteeing numerical stability in nonlinear finite element implementations. This property is critical not only for quasi-static simulations but also for dynamic scenarios where the preservation of hyperbolicity and stability of wave propagation is essential. The proposed model retains frame indifference, adheres to all three laws of thermodynamics, and seamlessly bridges scales from small-strain linear thermoelasticity to finite deformation regimes. It captures key features such as the nonlinear stress–temperature coupling seen in rubber-like materials (Ogden, 1992; Holzapfel and Simo, 1996), the entropic elasticity of polymers (Miehe, 1995), and the softening of melting transitions. Explicit forms of the free energy potentials are constructed to satisfy polyconvexity while remaining straightforward to implement in modern computational frameworks. As such, the formulation offers a robust, thermodynamically grounded foundation for simulating a broad class of thermomechanical problems, including those involving extreme thermal and mechanical loading.

The remainder of the paper is brokendown as follows. Section 2 presents the fundamentals of the kinematics and thermoelasticity of deformable solids. Internal energy and free energy densities are defined and state-of-the-art stability conditions for current thermoelastic models are presented. The section concludes with the introduction of the Third Law of thermodynamics and its consequences in relation to the definition of the specific heat coefficient. Section 3 presents a new theory of thermoelasticity compatible with the Third Law of thermodynamics, where the specific heat is shown to depend on both deformation and temperature, agreeing thus with existing experimental evidence. A multiplicative formulation for the specific heat is then presented in terms of deformation and temperature contributions, allowing for the explicit definition of the free energy density potential. Section 4 puts forward a volumetric–isochoric decomposition of the free energy density, with a comprehensive range of constitutive models applicable to a wide range of materials, including isotropic metals and rubbers. Section 5 summarises some concluding remarks. Appendix A revisits an important proposition for the stability of thermoelastic models when expressed in terms of either entropy or temperature. For completeness, Appendix B demonstrates the polyconvexity of the proposed thermoelastic model when expressed in terms of deformation and entropy.

2. Kinematics and thermodynamics description

2.1. The reference and current states

Consider the thermomechanical deformation of a solid from a reference configuration $\mathcal{B}_R$ (occupying a volume V_R of boundary ∂V_R and outward unit normal $\boldsymbol{N}$) to a current configuration at time t defined by $\mathcal{B}_t$ (occupying a volume v_t of boundary ∂v_t and outward unit normal $\boldsymbol{n}$), as shown in Fig. 1. The deformation between these configurations is described by a mapping function $\boldsymbol{x} = \boldsymbol{\phi}(\boldsymbol{X}, t)$ which maps material particles from their initial (reference) position $\boldsymbol{X} \in \mathcal{B}_R$ to their current position $\boldsymbol{x} \in \mathcal{B}_t$. Assuming sufficient regularity of the mapping $\boldsymbol{\phi}$, the deformation state of the body is described by the so-called fibre map $\boldsymbol{F}$ (mapping differential line vectors $d\boldsymbol{X}$ and $d\boldsymbol{x}$), area map $\boldsymbol{H}$ (mapping differential area vectors $d\boldsymbol{A}$ and $d\boldsymbol{a}$) and volume map J (mapping differential volume elements dV and dv) given as

$$\boldsymbol{F} = \frac{\partial \boldsymbol{\phi}}{\partial \boldsymbol{X}}; \qquad \boldsymbol{H} = \frac{1}{2}\boldsymbol{F} \times \boldsymbol{F}; \qquad J = \frac{1}{3}\boldsymbol{H} : \boldsymbol{F} = \det \boldsymbol{F}, \tag{1a,b,c}$$

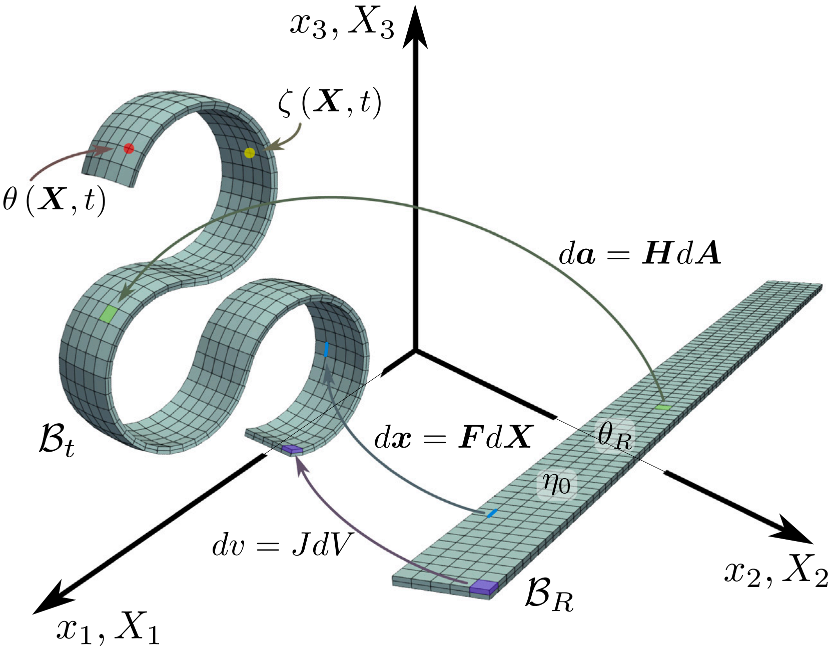

Fig. 1. Reference configuration $\mathcal{B}_R$ and current configuration $\mathcal{B}_t$ at time instant t with definition of thermoelastic variables: fibre map $\boldsymbol{F}$, area map $\boldsymbol{H}$, volume map J, temperature θ and entropy ζ.

where the tensor cross product $\times$ notation described in Gibbs and Wilson (1901), de Boer (1982), Bonet et al. (2015, 2016a) has been used (refer to Fig. 1). For simplicity, the triplet of kinematic fields in (1) is collected into the set $\boldsymbol{\mathcal{X}} = \{\boldsymbol{F}, \boldsymbol{H}, J\}$ in line with the notation used in Bonet et al. (2021b). Note that at the reference configuration $\boldsymbol{\mathcal{X}}_R = \{\boldsymbol{I}, \boldsymbol{I}, 1\}$ where $\boldsymbol{I}$ is the second order identity tensor, that is, the reference configuration is considered to be undeformed.

It will be assumed that the thermal state of the body is defined by a uniform reference temperature θ_R at $\mathcal{B}_R$ and at a current temperature $\theta(\boldsymbol{X}, t)$ at $\mathcal{B}_t$. Alternatively, the entropy per unit reference volume $\zeta(\boldsymbol{X}, t)$ at $\mathcal{B}_t$ can be used to describe the thermal state. In this case, it will be assumed that $\zeta = \eta_0$ represents the uniform entropy at the reference undeformed configuration (refer to Fig. 1). Note that deformation changes, including those due to thermal expansion, are measured from the reference configuration $\mathcal{B}_R$, which for simplicity will be assumed to be stress free. The full thermomechanical state can be therefore described by either the extended set $\boldsymbol{\mathcal{X}}_\zeta = \{\boldsymbol{\mathcal{X}}, \zeta\}$ or $\boldsymbol{\mathcal{X}}_\theta = \{\boldsymbol{\mathcal{X}}, \theta\}$.

2.2. Internal energy and complementary energy potentials

In thermoelasticity, the internal energy per unit undeformed volume $\mathscr{E}(\boldsymbol{X}, t)$, defined as the total energy minus the kinetic energy component, is a function of position $\boldsymbol{X}$, deformation state $\boldsymbol{F}$ and entropy ζ as $\mathscr{E}(\boldsymbol{X}, t) = \mathcal{E}(\boldsymbol{F}, \zeta, \boldsymbol{X})$, where the notation $\mathscr{E}$ and $\mathcal{E}$ is used to denote the same internal energy density with different functional dependency. Hyperbolicity, or existence and propagation of real wave speeds (Gurtin et al., 2009; Bonet et al., 2021a), is ensured by satisfying the so-called polyconvexity condition (Ball, 1976; Šilhavý, 1997)

$$\mathcal{E}(\boldsymbol{F}, \zeta, \boldsymbol{X}) = W(\boldsymbol{\mathcal{X}}_\zeta), \tag{2}$$

where W denotes a (not necessarily unique) polyconvex function with respect to the fields in the extended set $\boldsymbol{\mathcal{X}}_\zeta$, where the dependency with respect to the material particle $\boldsymbol{X}$ has been ignored for simplicity. The classical Coleman–Noll procedure (Coleman and Noll, 1963) enables the first Piola–Kirchhoff stress tensor $\mathbf{P}(\boldsymbol{X}, t) = \boldsymbol{\mathcal{P}}(\boldsymbol{F}, \zeta)$ and the temperature $\theta(\boldsymbol{X}, t) = \Theta(\boldsymbol{F}, \zeta)$ to be determined as

$$\boldsymbol{\mathcal{P}}(\boldsymbol{F}, \zeta) = \frac{\partial \mathcal{E}}{\partial \boldsymbol{F}}; \qquad \Theta(\boldsymbol{F}, \zeta) = \frac{\partial \mathcal{E}}{\partial \zeta}, \tag{3a,b}$$

where the notation $\{\mathbf{P}, \theta\}$ and $\{\boldsymbol{\mathcal{P}}, \Theta\}$ has been used to denote the same first Piola–Kirchhoff stress and temperature albeit with different functional dependency. Satisfaction of the above polyconvexity condition (2) ensures the one to one relationship between entropy ζ and temperature θ, such that the former can be expressed as a function of the latter and deformation, as $\zeta(\boldsymbol{X}, t) = \eta(\boldsymbol{F}, \theta)$ where ζ and η represent the same entropy albeit with different functional dependency. In addition, the stress free initial configuration at temperature θ_R implies

$$\theta_R = \Theta(\boldsymbol{I}, \eta_0); \qquad \boldsymbol{\mathcal{P}}(\boldsymbol{I}, \eta_0) = \mathbf{0}, \tag{4a,b}$$

where recall that η_0 denotes the value of entropy at the initial unstressed reference configuration where $\{\boldsymbol{F} = \boldsymbol{I}, \theta = \theta_R\}$. The thermal behaviour of the material is further determined by the definition of the specific heat coefficient $C_v(\boldsymbol{X}, t) = c_v(\boldsymbol{F}, \theta)$ per unit reference volume defined as

$$\begin{aligned} c_v &:= \left.\frac{d\mathscr{E}}{d\theta}\right|_{\boldsymbol{F}=\text{constant}} \\ &= \frac{\partial \mathcal{E}}{\partial \zeta}\frac{\partial \eta}{\partial \theta} = \theta \frac{\partial \eta}{\partial \theta}, \end{aligned} \tag{5}$$

where Eq. (3)$_b$ has been used in the second line above. In order to facilitate the use of temperature θ instead of entropy ζ as thermal variable, a partial Legendre transform is used to define the Helmholtz's free energy $\Psi(\boldsymbol{F}, \theta)$ as

$$\Psi(\boldsymbol{F}, \theta) = \mathcal{E}(\boldsymbol{F}, \eta(\boldsymbol{F}, \theta)) - \theta\eta(\boldsymbol{F}, \theta), \tag{6}$$

so that

$$\boldsymbol{P}(\boldsymbol{F}, \theta) = \frac{\partial \Psi}{\partial \boldsymbol{F}}; \qquad \eta(\boldsymbol{F}, \theta) = -\frac{\partial \Psi}{\partial \theta}; \qquad c_v(\boldsymbol{F}, \theta) = -\theta \frac{\partial^2 \Psi}{\partial \theta \partial \theta} = \theta \frac{\partial \eta}{\partial \theta}, \tag{7a,b,c}$$

where $\boldsymbol{P}(\boldsymbol{F}, \theta)$ symbolises an alternative functional dependency of the first Piola–Kirchhoff stress tensor in terms of $\boldsymbol{F}$ and θ.

Crucially, as shown in Šilhavý (1997) (**Proposition 17.5.8**), it is possible to demonstrate that polyconvexity of the internal energy density $\mathcal{E}$ (that is, W) with respect to the fields in $\boldsymbol{\mathcal{X}}_\zeta$ is equivalent to imposing polyconvexity of Ψ with respect to deformation fields $\boldsymbol{\mathcal{X}}$ and concavity with respect to the temperature θ. Appendix A includes a demonstration of this proposition for completeness adapted to the notation used throughout this paper.

Concavity of the Helmholtz's free energy function Ψ with respect to the temperature θ is simply achieved ensuring that $c_v \geq 0$ (refer to (7)$_c$). The integration with respect to θ of Eq. (5) gives the entropy expression as

$$\eta(\boldsymbol{F}, \theta) = \eta_R(\boldsymbol{F}) + \int_{\theta_R}^{\theta} \frac{c_v}{\vartheta} d\vartheta, \tag{8}$$

where $\eta_R(\boldsymbol{F})$ denotes the entropy density at reference temperature θ_R. Referring to Eq. (7)$_b$, above Eq. (8) can be integrated to yield the Helmholtz's free energy as

$$\begin{aligned} \Psi(\boldsymbol{F}, \theta) &= \Psi_R(\boldsymbol{F}) - \Delta\theta\eta_R(\boldsymbol{F}) - \int_{\theta_R}^{\theta} \left[\int_{\theta_R}^{\vartheta} \frac{c_v}{\xi} d\xi\right] d\vartheta \\ &= \Psi_R(\boldsymbol{F}) - \Delta\theta\eta_R(\boldsymbol{F}) - \theta \int_{\theta_R}^{\theta} \frac{c_v}{\vartheta} d\vartheta + \int_{\theta_R}^{\theta} c_v d\vartheta \\ &= \Psi_R(\boldsymbol{F}) - \Delta\theta\eta_R(\boldsymbol{F}) + \int_{\theta_R}^{\theta} c_v \left(1 - \frac{\theta}{\vartheta}\right) d\vartheta, \end{aligned} \tag{9}$$

where $\Psi_R(\boldsymbol{F})$ denotes the Helmholtz's free energy function at reference temperature θ_R and $\Delta\theta = \theta - \theta_R$ is the increment in temperature. Note that integration by parts has been used to transform the double integral in the last term of above Eq. (9). Eq. (9) is the common general expression used in thermoelasticity. In the case of a specific heat independent of the deformation, the first Piola–Kirchhoff stress tensor can be obtained as

$$\boldsymbol{P}(\boldsymbol{F}, \theta) = \frac{\partial \Psi_R}{\partial \boldsymbol{F}} - \Delta\theta \frac{\partial \eta_R}{\partial \boldsymbol{F}}, \tag{10}$$

which can be seen to depend linearly on the temperature. Making now use of the Legendre transform at reference temperature, namely

$$\Psi_R(\boldsymbol{F}) = \mathcal{E}_R(\boldsymbol{F}) - \theta_R\eta_R(\boldsymbol{F}), \tag{11}$$

where $\mathcal{E}_R(\boldsymbol{F})$ is the internal energy at reference temperature, the Helmholtz's free energy function can also be written as

$$\Psi(\boldsymbol{F}, \theta) = \mathcal{E}_R(\boldsymbol{F}) - \theta\eta_R(\boldsymbol{F}) + \int_{\theta_R}^{\theta} c_v \left(1 - \frac{\theta}{\vartheta}\right) d\vartheta, \tag{12}$$

or

$$\Psi(\boldsymbol{F}, \theta) = \frac{\theta}{\theta_R}\Psi_R(\boldsymbol{F}) - \left(\frac{\theta}{\theta_R} - 1\right)\mathcal{E}_R(\boldsymbol{F}) + \int_{\theta_R}^{\theta} c_v \left(1 - \frac{\theta}{\vartheta}\right) d\vartheta. \tag{13}$$

Eq. (13) is the classical expression used by Chadwick (1974) in the context of rubber elasticity, whereas Eq. (12) is useful to illustrate sufficient stability conditions needed to ensure the existence and propagation of real wave speeds (Ball, 1976; Šilhavý, 1997; Bonet et al., 2021a).

Specifically, sufficient conditions for polyconvexity of $\mathcal{E}$ with respect to the extended set $\boldsymbol{\mathcal{X}}_\zeta$ or, equivalently, polyconvexity and concavity requirements of $\Psi(\boldsymbol{F}, \theta)$ with respect to $\boldsymbol{\mathcal{X}}$ and θ, respectively, are guaranteed (Bonet et al., 2021b) (**Proposition 1**) provided that:

(i) $\mathcal{E}_R(\boldsymbol{F})$ is polyconvex in $\boldsymbol{\mathcal{X}}$,
(ii) $-\eta_R(\boldsymbol{F})$ can be expressed as a polyconvex function of $\boldsymbol{\mathcal{X}}$,

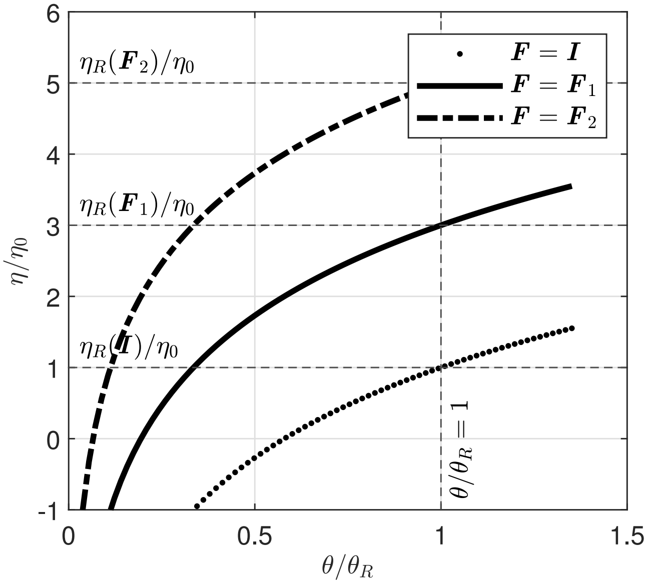

Fig. 2. Dimensionless relationship between temperature θ and entropy η at different values of the deformation gradient tensor and for a constant specific heat coefficient c_v^0.

(iii) c_v is positive and at most varies with the temperature θ.[1]

Typically, the specific heat coefficient c_v is assumed to be constant (i.e. $c_v = c_v^0$), where $c_v^0 \in \mathbb{R}^+$ for the range of temperatures of interest, resulting in an explicit closed-form expression for the entropy density and the Helmholtz's free energy density function as

$$\eta(\boldsymbol{F},\theta) = \eta_R(\boldsymbol{F}) + c_v^0 \ln\frac{\theta}{\theta_R}, \tag{14}$$

and

$$\Psi(\boldsymbol{F},\theta) = \Psi_R(\boldsymbol{F}) - \Delta\theta\eta_R(\boldsymbol{F}) + c_v^0\left(\Delta\theta - \theta\ln\frac{\theta}{\theta_R}\right). \tag{15}$$

The model defined above (14)–(15) is commonly used in the literature (Šilhavý, 1997; Gurtin et al., 2009; Holzapfel, 2000; Bonet et al., 2021a) for given choices of the pair $\{\Psi_R(\boldsymbol{F}), \eta_R(\boldsymbol{F})\}$. Notice that exploiting the use of (11), it is possible to work in terms of the alternative pairs $\{\mathcal{E}_R(\boldsymbol{F}), \eta_R(\boldsymbol{F})\}$ or $\{\mathcal{E}_R(\boldsymbol{F}), \Psi_R(\boldsymbol{F})\}$.

2.3. The third law of thermodynamics and its consequences

The Third Law of thermodynamics establishes that "*the entropy of a body should be zero at Kelvin state (zero temperature)*" (Callen, 1985; Ericksen, 1998). Clearly, this is incompatible with the choice of a constant specific heat coefficient c_v^0 as shown by Eq. (14), where $\lim_{\theta\to 0^+}\eta = -\infty$. This relationship between the entropy η and the temperature θ for constant specific heat c_v^0 is graphically displayed in Fig. 2. Consequently, the Third Law implies that the specific heat c_v must, at least, be a function of θ as $c_v(\theta)$. However, it is easy to show that this dependency alone is not sufficient to ensure a coupled thermomechanical model. In order to show this, note that using the Third Law together with Eq. (8) implies that

$$\eta_R(\boldsymbol{F}) = \int_0^{\theta_R} \frac{c_v(\vartheta)}{\vartheta}\, d\vartheta = \eta_0, \tag{16}$$

where η_0 is a constant value irrespective of the value of the deformation gradient $\boldsymbol{F}$, leading to

$$\Psi(\boldsymbol{F},\theta) = \Psi_R(\boldsymbol{F}) - \Delta\theta\eta_0 + \int_\theta^{\theta_R} c_v(\theta)\left(1 - \frac{\theta}{\vartheta}\right) d\vartheta. \tag{17}$$

In this Eq. (17), it can be noticed that the deformation and temperature dependent components are uncoupled. Therefore, defining a thermoelastic model that exhibits "*truly*" thermomechanical coupling and compatibility with the Third Law in the finite

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[1] Bonet et al. (2021b) only considered the case of constant specific heat c_v^0. However, the case of temperature dependent specific heat $c_v(\theta)$ can be easily demonstrated by noticing that the second derivative of (12) with respect to θ yields $-c_v(\theta)/\theta \le 0$, hence ensuring concavity of Ψ with respect to θ and, equivalently, polyconvexity of $\mathcal{E}$ with respect to $\mathcal{X}_\zeta$.

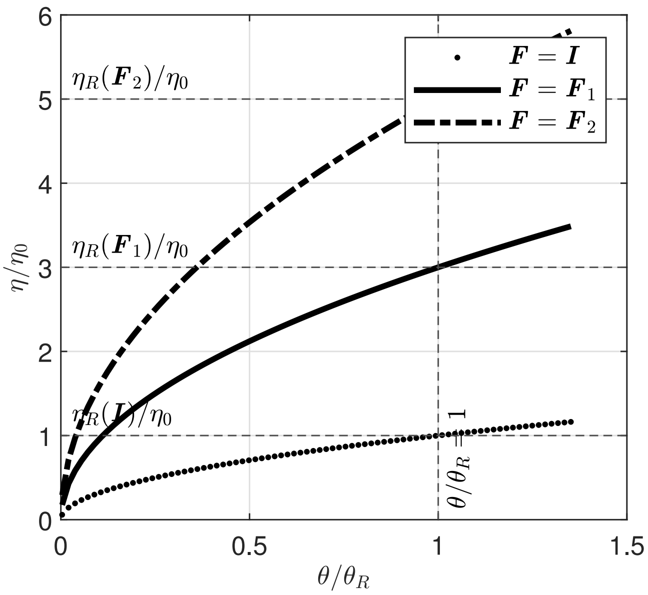

Fig. 3. Dimensionless qualitative description of the relationship between temperature θ and entropy η at different values of the deformation gradient in a compatible model with the Third Law of thermodynamics.

strain range necessitates a specific heat function of both temperature and deformation $c_v(\boldsymbol{F},\theta)$. Specific models of this dependency and the resulting thermomechanical equations will be described in the following section. These will lead to entropy–temperature relationships that are qualitatively depicted in Fig. 3.

3. Finite strain thermoelastic formulations compatible with the third law of thermodynamics

3.1. General case and convexity conditions

Consider a general thermoelastic constitutive model with a specific heat coefficient function of deformation and temperature which satisfies the conditions

$$c_v(\boldsymbol{F},\theta) \geq 0; \qquad c_v(\boldsymbol{I},\theta_R) = c_v^0, \tag{18a,b}$$

where $c_v^0 \in \mathbb{R}_{\geq 0}$ is the specific heat coefficient at the reference unstressed configuration. Assuming that the Third Law of thermodynamics is strictly adhered to (i.e. $\eta = 0$ for $\theta = 0$), the integration from $\theta = 0^{\text{o}}$K of Eq. (5) for the entropy and the internal energy density gives,

$$\eta(\boldsymbol{F},\theta) = \int_0^\theta \frac{c_v(\boldsymbol{F},\vartheta)}{\vartheta}\,d\vartheta; \qquad \mathcal{E}(\boldsymbol{F},\theta) = \mathcal{E}_K(\boldsymbol{F}) + \int_0^\theta c_v(\boldsymbol{F},\vartheta)d\vartheta, \tag{19a,b}$$

where $\mathcal{E}_K(\boldsymbol{F}) = \Psi_K(\boldsymbol{F})$ represents the internal energy or the Helmholtz's free energy density at the Kelvin state $\theta = 0^{\text{o}}$K and the subindex $(\bullet)_K$ is used to emphasise the Kelvin state condition. Notice that this identity can be easily verified when considering a partial Legendre transform between $\mathcal{E}$ and Ψ at the Kelvin state. It is important to realise that the entropy at the Kelvin state (i.e. $\eta = 0$) is not to be confused with the entropy present in the reference unstressed configuration (i.e. $\eta_0 = \eta(\boldsymbol{I},\theta_R)$, which is the reverse expression to that in $(4)_a$). Combination of the above equations in (19) yields the Helmholtz's free energy as

$$\Psi(\boldsymbol{F},\theta) = \Psi_K(\boldsymbol{F}) - \int_0^\theta c_v(\boldsymbol{F},\vartheta)\left(\frac{\theta}{\vartheta} - 1\right)d\vartheta. \tag{20}$$

Eq. (20) (by comparison with (17)) reinforces the earlier result that thermomechanical coupling necessarily implies that the specific heat coefficient c_v must be a function of the deformation $\boldsymbol{F}$, contrary to the traditional formulations. This further justifies the experimental evidence already reported in Nieto Simavilla et al. (2018), where it is shown that the specific heat is a function of deformation.

Another advantage of the representation in (20), is that necessary and sufficient conditions of convexity for $\Psi(\boldsymbol{F},\theta)$ can be easily identified. First, concavity with respect to θ is equivalent to requiring that $c_v(\boldsymbol{F},\theta) \geq 0$ for any deformation and temperature. Next, noting that the term inside the parenthesis within the integral on the right hand side of (20) is always positive, the polyconvexity of Ψ with respect to the extended set $\mathcal{X}$ at any temperature θ implies that both $\Psi_K(\boldsymbol{F})$ and $-c_v(\boldsymbol{F},\theta)$ are polyconvex with respect to the extended set $\boldsymbol{\mathcal{X}}$. Furthermore, it is possible to relate the above regularity requirements to those proposed by the authors in Bonet et al. (2021b) in terms of the internal energy and entropy at reference temperature $\mathcal{E}_R(\boldsymbol{F})$ and $-\eta_R(\boldsymbol{F})$, respectively, by noting that

$$\eta_R(\boldsymbol{F}) = \int_0^{\theta_R} \frac{c_v(\boldsymbol{F},\vartheta)}{\vartheta} d\theta; \qquad \mathcal{E}_R(\boldsymbol{F}) = \Psi_K(\boldsymbol{F}) + \int_0^{\theta_R} c_v(\boldsymbol{F},\vartheta) d\vartheta. \tag{21a,b}$$

From the above equations, it transpires that the polyconvexity of $-c_v(\boldsymbol{F},\theta)$ with respect to the extended set $\boldsymbol{\mathcal{X}}$ is equivalent to the polyconvexity of $-\eta_R(\boldsymbol{F})$ with respect to the extended set $\boldsymbol{\mathcal{X}}$. Furthermore, polyconvexity of both $\mathcal{E}_R(\boldsymbol{F})$ and $-c_v(\boldsymbol{F},\theta)$ with respect to the extended set $\boldsymbol{\mathcal{X}}$ imply the polyconvexity of $\Psi_K(\boldsymbol{F})$. Therefore the stability conditions proposed by the authors in Bonet et al. (2021b) are still valid in the current context. Finally, note that the expressions for $\Psi(\boldsymbol{F},\theta)$ in terms of the pair $\{\Psi_R(\boldsymbol{F}),\eta_R(\boldsymbol{F})\}$ or the alternative pairs $\{\mathcal{E}_R(\boldsymbol{F}),\eta_R(\boldsymbol{F})\}$ or $\{\Psi_R(\boldsymbol{F}),\mathcal{E}_R(\boldsymbol{F})\}$ in Eqs. (9), (12) and (13), respectively, are still valid simply noting that the specific heat is now a joint function of both $\boldsymbol{F}$ and θ as $c_v(\boldsymbol{F},\theta)$.

3.2. *A multiplicative model for the specific heat function $c_v(\boldsymbol{F},\theta)$*

The derivations in the previous section are entirely general beyond relying on the strict enforcement of the Third Law of thermodynamics and a positive specific heat coefficient. In order to progress further towards a specific model, an assumption is made in relation to the dependency of c_v with respect to $\boldsymbol{F}$ and θ by considering a multiplicative decomposition as

$$c_v(\boldsymbol{F},\theta) = c_v^0 \mathcal{X}(\boldsymbol{F}) g(\theta); \qquad \mathcal{X}(\boldsymbol{I}) = 1; \qquad g(\theta_R) = 1, \tag{22a,b,c}$$

where c_v^0 represents the specific heat coefficient in the absence of deformation and at reference temperature θ_R, and $\mathcal{X} : GL^+(3) \to \mathbb{R}_{\geq 0}$ and $g : \mathbb{R}_{\geq 0} \to \mathbb{R}_{\geq 0}$ are two suitably defined functions.

Remark 1. Note that Eq. $(22)_a$ can be further generalised by means of an additive combination of n components (or species) as

$$c_v(\boldsymbol{F},\theta) = \sum_{i=1}^{n} c_v^i \mathcal{X}_i(\boldsymbol{F}) g_i(\theta); \qquad \sum_{i=1}^{n} c_v^i = c_v^0, \tag{23a,b}$$

where c_v^i is the specific heat coefficient at the reference unstressed configuration, and $\mathcal{X}_i : GL^+(3) \to \mathbb{R}_{\geq 0}$ and $g_i : \mathbb{R}_{\geq 0} \to \mathbb{R}_{\geq 0}$ are two suitably defined functions also fulfilling $(22)_{b,c}$.

Remark 2. Phase transformations can also be included through the above additive decomposition by means of additional terms in the form

$$c_v^T(\boldsymbol{F},\theta) = L_T(\boldsymbol{F}) \delta(\theta - \theta_T), \tag{24}$$

where θ_T is the transition temperature, δ is the Dirac delta distribution[2] and L_T denotes the latent heat that may or may not depend on $\boldsymbol{F}$.

The substitution of the multiplicative decomposition $(22)_a$ into Eq. $(21)_a$ for $\eta_R(\boldsymbol{F})$ gives

$$\eta_R(\boldsymbol{F}) = c_v^0 \mathcal{X}(\boldsymbol{F}) \xi_R; \qquad \xi_R = \int_0^{\theta_R} \frac{g(\vartheta)}{\vartheta} d\vartheta. \tag{25a,b}$$

Consequently, the specific heat coefficient in $(22)_a$ and the reference entropy $\eta_R(\boldsymbol{F})$ in $(25)_a$ are related as

$$c_v(\boldsymbol{F},\theta) = \frac{1}{\xi_R} \eta_R(\boldsymbol{F}) g(\theta), \tag{26}$$

which bypasses the definition of the function $\mathcal{X}(\boldsymbol{F})$ via the reference entropy function $\eta_R(\boldsymbol{F})$ (i.e. $\mathcal{X}(\boldsymbol{F}) = \frac{1}{\xi_R c_v^0} \eta_R(\boldsymbol{F})$), and thus the Helmholtz's free energy can be variously expressed as

$$\Psi(\boldsymbol{F},\theta) = \Psi_K(\boldsymbol{F}) - \frac{\eta_R(\boldsymbol{F})}{\xi_R} \int_0^{\theta} g(\vartheta) \left(\frac{\theta}{\vartheta} - 1 \right) d\vartheta, \tag{27a}$$

$$\Psi(\boldsymbol{F},\theta) = \Psi_R(\boldsymbol{F}) - \eta_R(\boldsymbol{F}) \left(\Delta\theta - \frac{1}{\xi_R} \int_{\theta_R}^{\theta} g(\vartheta) \left(\frac{\theta}{\vartheta} - 1 \right) d\vartheta \right). \tag{27b}$$

Note that in clear contrast with Eq. (9), the thermomechanical term $\eta_R(\boldsymbol{F})$ now multiplies both the temperature change $\Delta\theta$ and the thermal integral featuring in Eq. (27b). As a consequence, the stresses are not any more limited to depend linearly on the temperature, increasing thus the range of application of the new model with respect to the classical one. Finally, the equation for the entropy (via simple differentiation of (27a) with respect to the temperature) becomes

$$\eta(\boldsymbol{F},\theta) = \eta_R(\boldsymbol{F}) G(\theta); \qquad G(\theta) = \frac{1}{\xi_R} \int_0^{\theta} \frac{g(\vartheta)}{\vartheta} d\vartheta. \tag{28a,b}$$

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[2] Or a suitably defined smooth counterpart function.

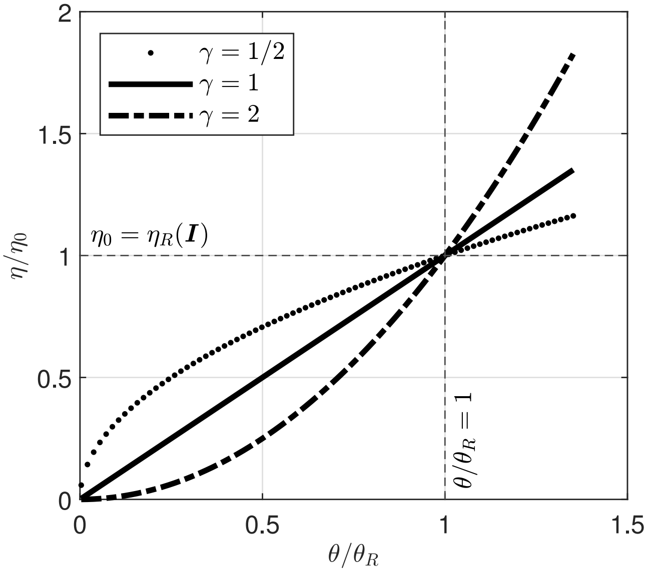

Fig. 4. Graphical dimensionless representation of the thermoelastic model for different values of the γ coefficient: temperature θ versus entropy η.

In above Eq. (28) it is straightforward to verify that $\eta(\boldsymbol{I}, \theta_R) = \eta_R(\boldsymbol{I}) = \eta_0$ and that $\eta(\boldsymbol{F}, 0) = 0$. In order to progress further, it is necessary to propose a specific function $g(\theta)$ such that the integrals above are analytical and accept a closed-form expression. With this in mind, consider the simple case

$$g(\theta) = \left(\frac{\theta}{\theta_R}\right)^{\gamma}; \qquad \gamma > 0, \tag{29}$$

where $\gamma \in \mathbb{R}^+$ is a material parameter. Note that this type of thermal dependency of c_v with respect to the temperature is often used in solid state physics and some gas models in statistical quantum thermodynamics (i.e. Debye model Kittel, 2005). However, it is assumed here without further physical explanation with the aim of reaching a simple analytical model. More complex behaviours may be modelled by use of additive decomposition as shown in Remark 1 above. With the choice of thermal dependency of c_v described in (26) and (29), the above integrals $(25)_b$ and $(28)_b$ can be evaluated analytically, resulting in

$$\xi_R = \int_0^{\theta_R} \frac{1}{\vartheta}\left(\frac{\vartheta}{\theta_R}\right)^{\gamma} d\vartheta = \frac{1}{\gamma}; \qquad G(\theta) = \frac{1}{\xi_R}\int_0^{\theta} \frac{1}{\vartheta}\left(\frac{\vartheta}{\theta_R}\right)^{\gamma} d\vartheta = \left(\frac{\theta}{\theta_R}\right)^{\gamma}, \tag{30a,b}$$

and therefore

$$c_v(\boldsymbol{F}, \theta) = \gamma \eta_R(\boldsymbol{F})\left(\frac{\theta}{\theta_R}\right)^{\gamma}; \qquad \eta = \eta_R(\boldsymbol{F})\left(\frac{\theta}{\theta_R}\right)^{\gamma}, \tag{31a,b}$$

where it is straightforward to show the relationship between the specific heat and the reference entropy at the unstressed state, that is

$$c_v^0 = c_v(\boldsymbol{I}, \theta_R) = \gamma \eta_0 = \gamma \eta_R(\boldsymbol{I}). \tag{32}$$

Fig. 4 shows a graphical representation of Eq. $(31)_b$ for different values of the material parameter $\gamma = \{1/2, 1, 2\}$. Choice of this parameter must be made experimentally through appropriate calibration, depending on the material under consideration.

In addition, the Helmholtz's free energy function can now be expressed in terms of $\eta_R(\boldsymbol{F})$ and the internal energy at the Kelvin state (i.e. $\theta = 0^{\circ}$K), $\Psi_K(\boldsymbol{F})$, as

$$\Psi(\boldsymbol{F}, \theta) = \Psi_K(\boldsymbol{F}) - \frac{\eta_R(\boldsymbol{F})\theta_R}{\gamma+1}\left(\frac{\theta}{\theta_R}\right)^{\gamma+1}. \tag{33}$$

Alternatively, the Helmholtz's free energy density at temperature θ can be variously referred to the free energy density and the internal energy at reference temperature θ_R as

$$\Psi(\boldsymbol{F}, \theta) = \Psi_R(\boldsymbol{F}) - \frac{\eta_R(\boldsymbol{F})\theta_R}{\gamma+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\gamma+1} - 1\right], \tag{34a}$$

$$\Psi(\boldsymbol{F}, \theta) = \mathcal{E}_R(\boldsymbol{F}) - \frac{\eta_R(\boldsymbol{F})\theta_R}{\gamma+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\gamma+1} + \gamma\right]. \tag{34b}$$

Particular choices of the coupling function $\eta_R(\boldsymbol{F})$ that model different types of thermoelastic behaviour will be presented in the following section. Finally, notice that an alternative representation of the free energy density can be written in terms of the internal and free energy at reference temperature as

$$\Psi(\boldsymbol{F},\theta) = \frac{\Psi_R(\boldsymbol{F})}{\gamma+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\gamma+1} + \gamma\right] - \frac{\mathcal{E}_R(\boldsymbol{F})}{\gamma+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\gamma+1} - 1\right]. \tag{35}$$

4. Volumetric–isochoric decomposition

In order to develop specific thermoelastic constitutive models, it is common practice and convenient to separate the volumetric component of the deformation given by J from the isochoric component given by $\hat{\boldsymbol{F}} = J^{-1/3}\boldsymbol{F}$, so that by construction $\det\hat{\boldsymbol{F}} = 1$ (Bonet et al., 2016b). Thermodynamic variables can then be expressed in terms of J and $\hat{\boldsymbol{F}}$ as shown below.

4.1. Additive decomposition of thermomechanic variables

Consider the standard split of the Helmholtz's free energy density into volumetric and isochoric components as

$$\Psi(\boldsymbol{F},\theta) = \underbrace{\bar{\Psi}(J,\theta)}_{\text{volumetric}} + \underbrace{\hat{\Psi}(\hat{\boldsymbol{F}},\theta)}_{\text{deviatoric}}, \tag{36}$$

so that the stress is now evaluated via $(7)_a$ introducing the pressure p and the deviatoric component of the first Piola–Kirchhoff stress tensor (Bonet et al., 2016b) as

$$\boldsymbol{P}(\boldsymbol{F},\theta) = \frac{\partial\Psi}{\partial\boldsymbol{F}} = \underbrace{pJ\boldsymbol{F}^{-T}}_{\text{volumetric}} + \underbrace{\hat{\boldsymbol{P}}}_{\text{deviatoric}}; \qquad p(J,\theta) = \frac{\partial\bar{\Psi}}{\partial J}; \qquad \hat{\boldsymbol{P}}(\boldsymbol{F},\theta) = \frac{\partial\hat{\Psi}}{\partial\boldsymbol{F}}. \tag{37a,b,c}$$

Note that the sign convention typically preferred for solids is used for the pressure definition p, that is $p > 0$ implies tension. Similarly, the differentiation of Eq. (36) with respect to the temperature via $(7)_b$ leads to a decomposition of the entropy as

$$\eta(\boldsymbol{F},\theta) = -\frac{\partial\Psi}{\partial\theta} = \underbrace{\bar{\eta}(J,\theta)}_{\text{volumetric}} + \underbrace{\hat{\eta}(\hat{\boldsymbol{F}},\theta)}_{\text{deviatoric}}; \qquad \bar{\eta}(J,\theta) = -\frac{\partial\bar{\Psi}}{\partial\theta}; \qquad \hat{\eta}(\hat{\boldsymbol{F}},\theta) = -\frac{\partial\hat{\Psi}}{\partial\theta}. \tag{38a,b,c}$$

In addition, a further differentiation with respect to θ via $(7)_c$ gives the decomposition of the specific heat coefficient as

$$c_v(\boldsymbol{F},\theta) = -\theta\frac{\partial^2\Psi}{\partial\theta\partial\theta} = \bar{c}_v(J,\theta) + \hat{c}_v(\hat{\boldsymbol{F}},\theta); \qquad \bar{c}_v(J,\theta) = \theta\frac{\partial\bar{\eta}}{\partial\theta}; \qquad \hat{c}_v(\hat{\boldsymbol{F}},\theta) = \theta\frac{\partial\hat{\eta}}{\partial\theta}. \tag{39a,b,c}$$

Note that Eq. $(39)_a$ represents a particular case of the general additive decomposition given in Eq. $(23)_a$, where for convenience the following split is assumed at the unstressed reference state

$$\bar{c}_v(1,\theta_R) = c_v^0; \qquad \hat{c}_v(\boldsymbol{I},\theta_R) = 0. \tag{40a,b}$$

Observe that the above process can also be followed in reverse, that is, starting from the assumption of the decomposition of the specific heat coefficient given in $(39)_a$ to obtain the volumetric isochoric split for the entropy and free energy density through successive temperature integration. The above decompositions of the free energy and entropy can also be taken at $\theta = \theta_R$ to give

$$\Psi_R(\boldsymbol{F}) = \bar{\Psi}_R(J) + \hat{\Psi}_R(\hat{\boldsymbol{F}}), \tag{41a}$$

$$\eta_R(\boldsymbol{F}) = \bar{\eta}_R(J) + \hat{\eta}_R(\hat{\boldsymbol{F}}), \tag{41b}$$

where in line with Eqs. $(40\text{a,b})_{a,b}$ the values of the reference entropy at the undeformed configuration will be taken as

$$\bar{\eta}_R(1) = \eta_0; \qquad \hat{\eta}_R(\boldsymbol{I}) = 0, \tag{42a,b}$$

so that relationship (32) holds. The sections below will present specific models for the volumetric and isochoric components of the free energy density, entropy and specific heat coefficient. The above volumetric–deviatoric decomposition leads to

$$\bar{c}_v(J,\theta) = \bar{\gamma}\bar{\eta}_R(J)\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}}; \qquad \hat{c}_v(\boldsymbol{F},\theta) = \hat{\gamma}\hat{\eta}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}} \tag{43a,b}$$

where $\bar{\gamma}, \hat{\gamma} \in \mathbb{R}^+$ are potentially different material parameters satisfying $\bar{\gamma}\eta_0 = c_v^0$.

4.2. Volumetric free energy density

In order to proceed further, it is necessary to propose specific functions for any two of the functions $\bar{\Psi}_R(J)$, $\bar{\mathcal{E}}_R(J)$ or $\bar{\eta}(J)$. In order to do so in a manner that is consistent with the stability (convexity) conditions, it is preferable to propose a convex function $\bar{\mathcal{E}}_R(J)$ and a concave function $\bar{\eta}_R(J)$. For instance, the following concave function is proposed for $\bar{\eta}_R(J)$,

$$\bar{\eta}_R(J) = \eta_0 + c_v^0\Gamma\frac{J^q - 1}{q}; \qquad 0 \le q \le 1, \tag{44}$$

where Γ is often referred to as the (positive) Mie–Grüneisen (Mie, 1903; Grüneisen, 1912) parameter and q is a dimensionless parameter. Note that the range of q ensures concavity of $\bar{\eta}_R$. The variation of the specific heat coefficient $\bar{c}_v$ with respect to the temperature will follow the model proposed in (43)$_a$. Moreover, in order to ensure stability, the simplest convex function for $\bar{\mathcal{E}}_R(J)$ can be chosen as

$$\bar{\mathcal{E}}_R(J) = U(J) + \beta(J-1); \qquad U(J) = \frac{1}{2}\kappa_R(J-1)^2, \tag{45a,b}$$

where κ_R is the bulk modulus at the reference temperature θ_R and β is a parameter to be chosen so that the reference pressure vanishes at $J = 1$. This implies

$$\left.\frac{\partial \bar{\Psi}_R}{\partial J}\right|_{J=1} = \left.\frac{\partial \bar{\mathcal{E}}_R}{\partial J}\right|_{J=1} - \theta_R \left.\frac{\partial \bar{\eta}_R}{\partial J}\right|_{J=1} = 0, \tag{46}$$

leading to

$$\beta = \Gamma c_v^0 \theta_R, \tag{47}$$

and a reference free energy

$$\bar{\Psi}_R(J) = U(J) + \Gamma c_v^0 \theta_R (J-1) - \theta_R \bar{\eta}_R(J); \qquad U(J) = \frac{1}{2}\kappa_R(J-1)^2, \tag{48a,b}$$

Remark 3. Note that above volumetric energy contribution $U(J) = \frac{1}{2}\kappa_R(J-1)^2$ in (45) and (48) can be enhanced by incorporating a *coercive* contribution which ensures the satisfaction of the growth conditions, namely, $U(J) \to +\infty$ as $J \to 0^+$ or $J \to +\infty$. With that in mind, the following options (Simo and Taylor, 1991; Miehe, 1994; Liu et al., 1994), amongst many reported in the literature, are possible

$$U(J) = \frac{\kappa_R}{4}(J^2 - 1 - 2\ln J); \tag{49a}$$

$$U(J) = \kappa_R(J - \ln J - 1); \tag{49b}$$

$$U(J) = \kappa_R(J \ln J - J + 1); \tag{49c}$$

which satisfy the growth conditions, are convex in J and also stress free at the origin. However, for the majority of applications where the Jacobian is not too far from the origin, the simplest expression in (45) and (48) can be safely used.

Consequently, substituting (44), (45) and (47) into (34b), the volumetric component of the free energy density is finally expressed as

$$\bar{\Psi}(J,\theta) = \frac{1}{2}\kappa_R(J-1)^2 + \Gamma c_v^0 \theta_R (J-1) - \frac{\theta_R}{\bar{\gamma}+1}\bar{\eta}_R(J)\left[\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}+1} + \bar{\gamma}\right], \tag{50}$$

and the corresponding pressure–temperature–volume equation of state is consistently obtained from (37)$_b$ as

$$p(J,\theta) = \kappa_R(J-1) + \Gamma c_v^0 \theta_R - \frac{\Gamma c_v^0 \theta_R J^{q-1}}{\bar{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}+1} + \bar{\gamma}\right]. \tag{51}$$

For the particular case $q = 1$, the above expression can be further simplified as

$$p(J,\theta) = \kappa_R(J-1) - \frac{\Gamma c_v^0 \theta_R}{\bar{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}+1} - 1\right]. \tag{52}$$

The above expression for the pressure (51) (or (52)) is no longer linear in θ, which was one of the desired aims of the proposed model. Finally, the Mie–Gruneisen parameter Γ can be related to the usual linear expansion coefficient α used in linearised thermoelasticity by noting that

$$\left.\frac{\partial p}{\partial \theta}\right|_{J=1,\theta=\theta_R} = -3\alpha\kappa_R = -\Gamma c_v^0, \tag{53}$$

and therefore

$$\Gamma = \frac{3\alpha\kappa_R}{c_v^0}. \tag{54}$$

In the above model, κ_R (the bulk modulus at $J = 1$ and $\theta = \theta_R$) and c_v^0 are material parameters, and $\bar{\gamma}$ and q are parameters that determine the nonlinearity of the model in relation to θ and J, respectively.

Remark 4. The choice of a convex function $\bar{\mathcal{E}}_R(J)$ and concave function $\bar{\eta}_R(J)$ (for $0 \leq q \leq 1$) ensures that the model stays convex for any temperature value. This can be easily confirmed by taking a further derivative of (51) with respect to J to give the temperature dependent bulk modulus as

$$\kappa = \kappa_R + (1-q)\frac{\Gamma c_v^0 \theta_R}{\bar{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}+1} + \bar{\gamma}\right] \geq 0. \tag{55}$$

Note that a simple choice of reference free energy such as $\bar{\Psi}_R(J) = \frac{1}{2}\kappa_R(J-1)^2$ (in comparison with (48)) would lead

$$\kappa = \kappa_R + (1-q)\frac{\Gamma c_v^0 \theta_R}{\bar{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}+1} - 1\right], \tag{56}$$

which, for $\theta < \theta_R$, will give bulk modulus below κ_R. In the limit $\theta = 0^{\text{o}}\text{K}$, stability is lost if

$$\kappa_R < (1-q)\frac{\Gamma c_v^0 \theta_R}{\bar{\gamma}+1}. \tag{57}$$

In contrast, the model proposed in (50) stays stable for any temperature provided that $\kappa_R > 0$, $0 \leq q \leq 1$ and all other parameters are positive.

4.3. Isochoric free energy density — simple models

For many materials, particularly isotropic metals, the coupling of mechanical and thermal effects only takes place in relation to the volumetric deformation. Such cases are simply described by

$$\hat{\Psi}(\boldsymbol{F},\theta) = \hat{\Psi}_R(\boldsymbol{F}); \qquad \hat{c}_v = 0; \qquad \hat{\eta}(\boldsymbol{F},\theta) = 0, \tag{58a,b,c}$$

where the choices $(58)_{b,c}$ satisfy $(43)_b$ and the isochoric strain energy can be specified by a variety of models in the literature (Gurtin et al., 2009; Bonet et al., 2016b; Holzapfel, 2000; Šilhavý, 1997), such as the well-known neo-Hookean strain energy as

$$\hat{\Psi}(\boldsymbol{F},\theta) = \hat{\Psi}_R(\boldsymbol{F}) = \hat{\Psi}_R^{\text{nH}}(\boldsymbol{F}) = \frac{1}{2}\mu_R(\hat{\boldsymbol{F}} : \hat{\boldsymbol{F}} - 3), \tag{59}$$

where in this case the deviatoric stress is independent of the temperature and the stress free condition is implicitly satisfied due to the isochoric nature of $\hat{\boldsymbol{F}}$ and μ_R is a positive material parameter. A slightly more sophisticated model can be developed in order to simulate material softening and melting at high temperatures, which are of great interest in the context of multi-material applications, that is, for the modelling of extreme deformations at very high temperatures (Bonet et al., 2021b). For instance, a bilinear model in which the material softens linearly beyond a certain transition temperature θ_T until it melts at temperature θ_M can be constructed by taking $\hat{c}_v = 0$, but

$$\hat{\eta}(\boldsymbol{F},\theta) = \begin{cases} 0 & \text{if} \quad \theta \leq \theta_T \\ \hat{\eta}_T(\boldsymbol{F}) & \text{if} \quad \theta_T < \theta \leq \theta_M. \end{cases} \tag{60}$$

Integrating the equation above with respect to θ gives

$$\hat{\Psi}(\boldsymbol{F},\theta) = \begin{cases} \hat{\Psi}_R(\boldsymbol{F}) & \text{if} \quad \theta \leq \theta_T \\ \hat{\Psi}_R(\boldsymbol{F}) - \hat{\eta}_T(\boldsymbol{F})(\theta - \theta_T) & \text{if} \quad \theta > \theta_T, \end{cases} \tag{61}$$

where by enforcing that the material model melts at $\theta = \theta_M$, that is $\hat{\Psi}(\boldsymbol{F},\theta_M) = 0$, gives

$$\hat{\eta}_T(\boldsymbol{F}) = \frac{\hat{\Psi}_R(\boldsymbol{F})}{\theta_M - \theta_T}, \tag{62}$$

and therefore

$$\hat{\Psi}(\boldsymbol{F},\theta) = \begin{cases} \hat{\Psi}_R(\boldsymbol{F}) & \text{if} \quad \theta \leq \theta_T \\ \left(\frac{\theta_M - \theta}{\theta_M - \theta_T}\right)\hat{\Psi}_R(\boldsymbol{F}) & \text{if} \quad \theta_T < \theta \leq \theta_M \\ 0 & \text{if} \quad \theta > \theta_M. \end{cases} \tag{63}$$

Note that in this case $\hat{\eta}_T(\boldsymbol{F})$ is in fact polyconvex rather than concave, but the resulting free energy function is polyconvex for $\theta \leq \theta_M$.

4.4. Nonlinear melting model

A more general nonlinear model of melting behaviour, also relevant in the context of multi-material modelling (Bonet et al., 2021b), can be constructed by following the temperature dependency described above in $(42)_b$ and in $(43)_b$ for the isochoric component of the specific heat coefficient, that is

$$\hat{c}_v = \hat{\gamma}\hat{\eta}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}}; \qquad \hat{\eta}_R(\boldsymbol{I}) = 0. \tag{64a,b}$$

Note that in this equation, $\hat{\gamma}$ does not need to be equal to $\bar{\gamma}$ (refer to (43)). The resulting free energy density expression is given by Eq. (34a) as

$$\hat{\Psi}(\boldsymbol{F},\theta) = \hat{\Psi}_R(\boldsymbol{F}) - \frac{\hat{\eta}_R(\boldsymbol{F})\theta_R}{\hat{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}+1} - 1\right]. \tag{65}$$

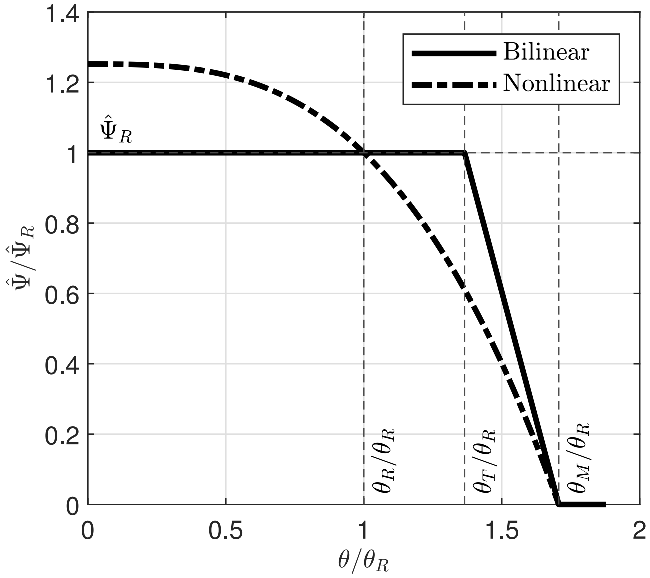

Fig. 5. Dimensionless graphical representation of the bilinear and nonlinear constitutive models for melting: temperature θ versus deviatoric free energy density $\hat{\Psi}$.

Enforcement of melting conditions at $\theta = \theta_M$ yields

$$\hat{\eta}_R(\boldsymbol{F}) = \frac{\hat{\gamma}+1}{\theta_R}\frac{\hat{\Psi}_R(\boldsymbol{F})}{\left(\theta_M/\theta_R\right)^{\hat{\gamma}+1}-1}, \tag{66}$$

which after substitution back into (65) results in the isochoric component of the free energy density as

$$\hat{\Psi}(\boldsymbol{F},\theta) = \frac{1-\left(\theta/\theta_M\right)^{\hat{\gamma}+1}}{1-\left(\theta_R/\theta_M\right)^{\hat{\gamma}+1}}\hat{\Psi}_R(\boldsymbol{F}). \tag{67}$$

Finally, for completeness, expressions (63) and (67) are shown in Fig. 5.

4.5. Modified entropic elasticity

The classical thermoelasticity model for rubber (Treloar, 1975) is based on a modified entropic elasticity assumption whereby the internal strain energy at the reference configuration is only a function of the volumetric deformation (Chadwick, 1974; Miehe, 1995). In the present context of an additive decomposition of energy functionals this can be implemented by adopting $\hat{\mathcal{E}}_K(\hat{\boldsymbol{F}}) = \hat{\Psi}_K(\hat{\boldsymbol{F}}) = 0$, so that $\mathcal{E}_K(\boldsymbol{F}) = \bar{\mathcal{E}}_K(J)$. The implication of this assumption, together with a variation of $\hat{c}_v$ with temperature in accordance with equations in (64) leads to (refer to (33))

$$\hat{\Psi}(\hat{\boldsymbol{F}},\theta) = -\frac{\hat{\eta}_R(\hat{\boldsymbol{F}})\theta_R}{\hat{\gamma}+1}\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}+1}, \tag{68}$$

and through consistent differentiation with respect to temperature

$$\hat{\eta}(\hat{\boldsymbol{F}},\theta) = \hat{\eta}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}}; \qquad \hat{c}_v(\hat{\boldsymbol{F}},\theta) = -\hat{\gamma}\hat{\eta}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}}, \tag{69a,b}$$

In addition, at the reference temperature $\theta = \theta_R$, Eq. (68) implies

$$\hat{\eta}_R(\hat{\boldsymbol{F}}) = -\frac{\hat{\gamma}+1}{\theta_R}\hat{\Psi}_R(\hat{\boldsymbol{F}}), \tag{70}$$

and finally,

$$\Psi(\hat{\boldsymbol{F}},\theta) = \hat{\Psi}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}+1}. \tag{71}$$

Note that Eq. (71) satisfies the polyconvexity condition with respect to $\boldsymbol{\mathcal{X}}$ provided that $\hat{\Psi}_R$ is polyconvex with respect to $\boldsymbol{\mathcal{X}}$. However, for standard hyperelastic models $\hat{\Psi}_R \geq 0$ and therefore

$$\hat{c}_v(\hat{\boldsymbol{F}},\theta) = -\frac{\hat{\gamma}(\hat{\gamma}+1)}{\theta_R}\hat{\Psi}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}} \leq 0. \tag{72}$$

In order to ensure that the complete model is physically valid, the total specific heat coefficient (i.e. $c_v(\boldsymbol{F},\theta) = \bar{c}_v(J,\theta) + \hat{c}_v(\hat{\boldsymbol{F}},\theta)$) must remain non-negative, that is

$$c_v(\boldsymbol{F},\theta) = \bar{\gamma}\bar{\eta}_R(J)\left(\frac{\theta}{\theta_R}\right)^{\bar{\gamma}} - \frac{\hat{\gamma}(\hat{\gamma}+1)}{\theta_R}\hat{\Psi}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}} \geq 0. \tag{73}$$

Assuming that $\bar{\gamma} = \hat{\gamma} = \gamma$ for simplicity, and considering that $J \approx 1$ given that rubber is nearly incompressible, and using Eqs. $(42)_a$ and (32), gives the restriction

$$\gamma(\gamma+1) \leq \frac{c_v^0\theta_R}{\hat{\Psi}_R^{\max}}, \tag{74}$$

where $\hat{\Psi}_R^{\max}$ denotes the maximum isochoric strain energy that can be achieved before material failure. For most rubber like materials, the restriction given by Eq. (74) is of little practical consequence. Indeed, considering usual material parameters as reported in Holzapfel (2000) for rubber, that is, $c_v^0 = 1.74 \times 10^6 \frac{\text{N}}{\text{m}^2\,\text{K}}$, $\theta_R = 293^o\text{K}$, $\mu_R = 4.225 \times 10^5 \frac{\text{N}}{\text{m}^2}$, and taking a neo-Hookean model (59) in which $\hat{\Psi}_R^{\max}$ is reached at a one dimensional stretch (i.e. plane stress conditions) of $\lambda_{\max} = 10$, it leads to a limit of $\gamma \leq 4.5$.

Remark 5. An alternative modified entropic elasticity model can be arrived at by taking $\hat{\mathcal{E}}_R(\hat{\boldsymbol{F}}) = 0$ instead of $\hat{\mathcal{E}}_K(\boldsymbol{F}) = 0$. It is easy to show that doing so (refer to Eq. (35)) leads to the alternative model

$$\hat{\Psi}(\hat{\boldsymbol{F}},\theta) = \frac{\hat{\Psi}_R(\hat{\boldsymbol{F}})}{\hat{\gamma}+1}\left[\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}+1} + \hat{\gamma}\right]. \tag{75}$$

Consistent differentiation with respect to the temperature gives

$$\hat{\eta}(\hat{\boldsymbol{F}},\theta) = -\frac{\hat{\Psi}_R(\hat{\boldsymbol{F}})}{\theta_R}\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}}; \qquad \hat{c}_v(\hat{\boldsymbol{F}},\theta) = -\frac{\hat{\gamma}}{\theta_R}\hat{\Psi}_R(\hat{\boldsymbol{F}})\left(\frac{\theta}{\theta_R}\right)^{\hat{\gamma}}. \tag{76a,b}$$

As in the above entropic elasticity model described in (68), $\hat{c}_v \leq 0$, and by comparison of $(76)_b$ with (72), it is possible to establish an analogous (albeit less restrictive) constraint to that in (74), that is

$$\gamma \leq \frac{c_v^0\theta_R}{\hat{\Psi}_R^{\max}}. \tag{77}$$

5. Conclusions

In this work, it has been shown that commonly used large strain thermoelastic models — where the specific heat coefficient is either constant or solely temperature-dependent — are fundamentally incompatible with the Third Law of Thermodynamics, which dictates that entropy must vanish as temperature approaches absolute zero. To resolve this inconsistency, it was demonstrated that the specific heat must also depend on deformation in order for meaningful thermomechanical coupling to exist within a thermodynamically consistent framework. Based on this insight, a simple yet robust constitutive model was proposed, in which the specific heat is formulated as a multiplicative combination of a deformation-dependent part and a temperature-dependent component. This model not only satisfies the Third Law but also fulfils the necessary convexity conditions to ensure the existence of real wave speeds, making it mechanically stable. Furthermore, it offers broad applicability: it recovers classical entropic elasticity models for rubber, is capable of capturing melting and softening behaviour, and converges to linear thermoelasticity relations in the small strain limit. Overall, the proposed framework provides a thermodynamically rigorous and physically meaningful extension of thermoelastic theory suitable for a wide range of material behaviours and deformation regimes.

Contrary to existing models whose range of applicability is limited, both in terms of deformation and temperature, the proposed thermo-mechanical framework has been constructed *ab initio* to circumvent these limitations, being valid from the Kelvin state all the way to melting, and for any value of deformation. Interestingly, the new framework has been constructed to make use of well-known material parameters, such as the specific heat at reference temperature and unit deformation, or the Mie–Grüneisen material parameter, with only one additional dimensionless material parameter γ (in the simplest possible case) that could be easily calibrated experimentally. Note that, in some cases, the new parameter γ can be related to existing models, such as the Debye model (Kittel, 2005) featuring in quantum thermodynamics, providing thus a sound thermo-mechanical foundation. The formulation is shown to straightforwardly grow in sophistication and complexity by considering both multiplicative and additive decompositions of the temperature-deformation dependent specific heat, which would naturally lead to a larger number of material parameters, based on the needs of the user.

CRediT authorship contribution statement

Javier Bonet: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Antonio J. Gil:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge funding received from grants PID2022-141957OB-C21 and PID2022-141957OA-C22 financed by MCIN/AEI /10.13039/501100011033/ FEDER, UE. A. J. Gil wishes to acknowledge the support provided by the Defence, Science and Technology Laboratory (Dstl) and The Leverhulme Trust Foundation (UK) through a Leverhulme Fellowship.

Appendix A. Alternative stability conditions in thermoelasticity in terms of entropy or temperature

Consider the internal energy density and the free energy density defined as

$$\mathcal{E}(\boldsymbol{F},\zeta) = W(\boldsymbol{\mathcal{X}},\zeta); \qquad \Psi(\boldsymbol{F},\theta) = \mathit{\Psi}(\boldsymbol{\mathcal{X}},\theta), \tag{78a,b}$$

where $\{\mathcal{E}, W\}$ and $\{\Psi, \mathit{\Psi}\}$ are used to indicate different functional dependencies of the internal and free energies, respectively. The entropy can thus be variously obtained as

$$\zeta = \eta(\boldsymbol{F},\theta) = -\frac{\partial \Psi}{\partial \theta} = -\frac{\partial \mathit{\Psi}}{\partial \theta} = \varsigma(\boldsymbol{\mathcal{X}},\theta). \tag{79}$$

Similarly, the temperature can be variously obtained as

$$\theta = \Theta(\boldsymbol{F},\zeta) = \frac{\partial \mathcal{E}}{\partial \zeta} = \frac{\partial W}{\partial \zeta} = \mathit{\Theta}(\boldsymbol{\mathcal{X}},\zeta). \tag{80}$$

Internal and free energy densities are related via the well-known partial Legendre transform

$$W(\boldsymbol{\mathcal{X}},\zeta) = \mathit{\Theta}(\boldsymbol{\mathcal{X}},\zeta)\zeta - \mathit{\Psi}(\boldsymbol{\mathcal{X}},\mathit{\Theta}(\boldsymbol{\mathcal{X}},\zeta)), \tag{81}$$

which is the counterpart expression of that presented in (6). The variation of entropy $\delta\zeta$ with respect to changes in deformation $\delta\boldsymbol{\mathcal{X}}$ and temperature $\delta\theta$ (refer to (79)) gives

$$\begin{aligned} \delta\zeta &= \frac{\partial \varsigma}{\partial \boldsymbol{\mathcal{X}}} \bullet \boldsymbol{\mathcal{X}} + \frac{\partial \varsigma}{\partial \theta}\delta\theta \\ &= -\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \boldsymbol{\mathcal{X}}} \bullet \boldsymbol{\mathcal{X}} - \frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\delta\theta, \end{aligned} \tag{82}$$

where the symbol • is used to represent a suitable inner product. It is now convenient to express the components of the Hessian of the internal energy W in terms of those of the free energy $\mathit{\Psi}$. The first partial derivatives of the internal energy are

$$\frac{\partial W}{\partial \boldsymbol{\mathcal{X}}} = \frac{\partial \mathit{\Psi}}{\partial \boldsymbol{\mathcal{X}}}; \qquad \frac{\partial W}{\partial \zeta} = \theta, \tag{83a,b}$$

from where the partial derivatives of the temperature can be obtained as

$$\frac{\partial \mathit{\Theta}}{\partial \zeta} = \left(\frac{\partial \eta}{\partial \theta}\right)^{-1} = -\left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\right)^{-1}, \tag{84a}$$

$$\frac{\partial \mathit{\Theta}}{\partial \boldsymbol{\mathcal{X}}} = \frac{\partial^2\, W}{\partial \boldsymbol{\mathcal{X}} \partial \zeta} = \frac{\partial}{\partial \zeta}\left(\frac{\partial W}{\partial \boldsymbol{\mathcal{X}}}\right) = -\left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\right)^{-1}\left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \boldsymbol{\mathcal{X}}}\right), \tag{84b}$$

and second,

$$\frac{\partial^2 W}{\partial \boldsymbol{\mathcal{X}} \partial \boldsymbol{\mathcal{X}}} = \frac{\partial^2 \mathit{\Psi}}{\partial \boldsymbol{\mathcal{X}} \partial \boldsymbol{\mathcal{X}}} - \left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\right)^{-1}\left(\frac{\partial^2 \mathit{\Psi}}{\partial \boldsymbol{\mathcal{X}} \partial \theta} \otimes \frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \boldsymbol{\mathcal{X}}}\right), \tag{85a}$$

$$\frac{\partial^2 W}{\partial \mathcal{S} \partial \boldsymbol{\mathcal{X}}} = -\left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\right)^{-1} \frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \boldsymbol{\mathcal{X}}} = \frac{\partial^2 W}{\partial \boldsymbol{\mathcal{X}} \partial \theta}, \tag{85b}$$

$$\frac{\partial^2 W}{\partial \zeta \partial \zeta} = -\left(\frac{\partial^2 \mathit{\Psi}}{\partial \theta \partial \theta}\right)^{-1}. \tag{85c}$$

With the purpose of relating stability conditions in terms of the internal and free energy densities, we compute

$$\mathcal{H} = \begin{bmatrix} \delta\boldsymbol{\mathcal{X}}\bullet & \delta\zeta \end{bmatrix} \begin{bmatrix} \frac{\partial^2 W}{\partial \boldsymbol{\mathcal{X}} \partial \boldsymbol{\mathcal{X}}} & \frac{\partial^2 W}{\partial \boldsymbol{\mathcal{X}} \partial \zeta} \\ \frac{\partial^2 W}{\partial \zeta \partial \boldsymbol{\mathcal{X}}} & \frac{\partial^2 W}{\partial \zeta \partial \zeta} \end{bmatrix} \begin{bmatrix} \bullet\delta\boldsymbol{\mathcal{X}} \\ \delta\zeta \end{bmatrix}, \tag{86}$$

and substituting (82) and (85) into above Eq. (86), and after some algebra, it yields

$$\mathcal{H} = \begin{bmatrix} \delta\boldsymbol{\mathcal{X}}\bullet & \delta\theta \end{bmatrix} \begin{bmatrix} \frac{\partial^2 \Psi}{\partial\boldsymbol{\mathcal{X}}\partial\boldsymbol{\mathcal{X}}} & \mathbf{0} \\ \mathbf{0} & -\frac{\partial^2\Psi}{\partial\theta\partial\theta} \end{bmatrix} \begin{bmatrix} \bullet\delta\boldsymbol{\mathcal{X}} \\ \delta\theta \end{bmatrix}. \tag{87}$$

Comparison between (86) and (87), it is straightforward to conclude that *"W is polyconvex in* $\{\boldsymbol{\mathcal{X}},\zeta\}$ *if and only if* Ψ *is polyconvex in* $\boldsymbol{\mathcal{X}}$ *and concave in* θ*"*.

Appendix B. Polyconvexity of the constitutive model in terms of the entropy

The proposed constitutive model in (33) or in its variants (34a)–(34b) can be re-formulated in terms of the internal energy $\mathcal{E}$ (or W) (refer to $(78)_a$). With that in mind, Eq. $(31)_b$ can be re-written to give the temperature in terms of the entropy as

$$\begin{aligned} \theta = \Theta(\boldsymbol{F},\zeta) &= \theta_R \left(\frac{\zeta}{\eta_R(\boldsymbol{F})}\right)^{\frac{1}{\gamma}} \\ &= \Theta(\boldsymbol{\mathcal{X}},\zeta) = \theta_R \left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\frac{1}{\gamma}}, \end{aligned} \tag{88}$$

where $\zeta_R(\boldsymbol{\mathcal{X}}) = \eta_R(\boldsymbol{F})$ is the entropy at reference temperature written in terms of alternative functional dependencies. Integration with respect to the entropy gives

$$\mathcal{E}(\boldsymbol{F},\zeta) = \mathcal{E}_R(\boldsymbol{F}) + \int_{\zeta_R}^{\zeta} \Theta(\boldsymbol{F},\bar{\zeta})d\bar{\zeta}; \qquad \text{or} \qquad W(\boldsymbol{\mathcal{X}},\zeta) = W_R(\boldsymbol{\mathcal{X}}) + \int_{\zeta_R}^{\zeta} \Theta(\boldsymbol{\mathcal{X}},\bar{\zeta})d\bar{\zeta}, \tag{89a,b}$$

where $\mathcal{E}_R(\boldsymbol{F}) = W_R(\boldsymbol{\mathcal{X}})$ represents the internal energy at reference temperature θ_R with alternative functional dependency, which for the specific expression in the second line of (88) yields

$$\begin{aligned} W(\boldsymbol{\mathcal{X}},\zeta) &= W_R(\boldsymbol{\mathcal{X}}) + \frac{\theta_R}{\left(\frac{1}{\gamma}+1\right)}\zeta_R(\boldsymbol{\mathcal{X}})\left(\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\frac{1}{\gamma}+1} - 1\right) \\ &= W_R(\boldsymbol{\mathcal{X}}) - \frac{\theta_R}{\left(\frac{1}{\gamma}+1\right)}\zeta_R(\boldsymbol{\mathcal{X}}) + \frac{\theta_R}{\left(\frac{1}{\gamma}+1\right)}\zeta^{\frac{1}{\gamma}+1}\left(\zeta_R(\boldsymbol{\mathcal{X}})\right)^{-\frac{1}{\gamma}}. \end{aligned} \tag{90}$$

It is now possible to demonstrate that sufficient conditions for the polyconvexity of W with respect to its arguments $\boldsymbol{\mathcal{X}},\zeta$ are polyconvexity of W_R and $-\zeta_R$ with respect to its argument $\boldsymbol{\mathcal{X}}$. Indeed, provided that W_R and $-\zeta_R$ are polyconvex, polyconvexity of W is hinged on the last term on the right hand side of (90). Rename $\alpha = \frac{1}{\gamma}$ and define $\mathcal{Y}(\boldsymbol{\mathcal{X}},\zeta) = \zeta^{\alpha+1}\left(\zeta_R(\boldsymbol{\mathcal{X}})\right)^{-\alpha}$, and note that polyconvexity of $\mathcal{Y}$ would imply polyconvexity of W. With that in mind, the first variation of $\mathcal{Y}$ gives

$$\delta\mathcal{Y} = (\alpha+1)\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha}\delta\zeta - \alpha\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha+1}\left(\frac{\partial\zeta_R(\boldsymbol{\mathcal{X}})}{\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right), \tag{91}$$

and the second variation gives

$$\begin{aligned} \delta^2\mathcal{Y} &= \alpha\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha+1}\left(\delta\boldsymbol{\mathcal{X}} : \frac{\partial^2(-\zeta_R(\boldsymbol{\mathcal{X}}))}{\partial\boldsymbol{\mathcal{X}}\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right) \\ &\quad + \frac{\alpha(\alpha+1)}{\zeta}\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha}\left((\delta\zeta)^2 - \frac{2\zeta\delta\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\left(\frac{\partial\zeta_R(\boldsymbol{\mathcal{X}})}{\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right) + \left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\left(\frac{\partial\zeta_R(\boldsymbol{\mathcal{X}})}{\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right)\right)^2\right) \\ &= \alpha\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha+1}\underbrace{\left(\delta\boldsymbol{\mathcal{X}} : \frac{\partial^2(-\zeta_R(\boldsymbol{\mathcal{X}}))}{\partial\boldsymbol{\mathcal{X}}\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right)}_{\geq 0} \\ &\quad + \frac{\alpha(\alpha+1)}{\zeta}\left(\frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\right)^{\alpha}\underbrace{\left(\delta\zeta - \frac{\zeta}{\zeta_R(\boldsymbol{\mathcal{X}})}\left(\frac{\partial\zeta_R(\boldsymbol{\mathcal{X}})}{\partial\boldsymbol{\mathcal{X}}} : \delta\boldsymbol{\mathcal{X}}\right)\right)^2}_{\geq 0}, \end{aligned} \tag{92}$$

and therefore $\delta^2\mathcal{Y} \geq 0$, which concludes that W is polyconvex with respect to $\{\boldsymbol{\mathcal{X}},\zeta\}$

Data availability

No data was used for the research described in the article.

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