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Coupling effects in dynamic calorimetry: Frequency-dependent relations for specific heat and thermomechanical responses — A one-dimensional approach based on thermodynamics with internal state variables

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ABSTRACT

As shown by Christensen et al. [2], temperature-induced stresses or strains can have a strong influence on the frequency-dependent specific heat, especially of thin layers of viscoelastic materials near the glass transition. Thus, both the mathematical representation and the physical understanding of these couplings are essential for the interpretation of temperature-modulated DSC data. The approach provided in this paper is based on thermodynamics with internal state variables. It thus differs from the transfer-matrix method which has been applied in Refs. [2,29] and constitutes a thermodynamic basis from a different point of view for the interpretation of the results obtained in Refs. [2,29,32]. Furthermore, although not the object of this paper, time-domain simulations can also be done with the model presented thus allowing for the calculation of temperature-ramping experiments and effects observed therein [42]. The approach in this paper is restricted to one-dimensional states of stress and strain to focus on the main idea and keep the mathematical formalism to a minimum. The Gibbs free energy is chosen as thermodynamic potential and the primary variables – the stress and the temperature – are supplemented by a set of internal state variables which is introduced to include history-dependent and hence viscoelastic effects. The Gibbs free energy is approximated up to second order terms in the vicinity of a reference state. Employing the Legendre transform, a corresponding expression for the Helmhotz free energy is obtained. Evaluating the laws of thermodynamics, explicit frequency-dependent expressions for the specific heat under constant stress or strain, the thermal expansion behaviour as well as the mechanical response functions are obtained. Recently published formulations of the Prigogine–Defay ratio can also be derived from the proposed constitutive model.

1. Introduction

If the temperature of a glass-forming substance is continuously reduced, the thermal motion of its molecules is decelerated more and more and eventually becomes "frozen in" such that, if crystallization is avoided, the material undergoes a glass transition and becomes an amorphous solid. The characteristic temperature under which the solid remains stable within observable time frames is the glass transition temperature. As the glass transition is a dynamic phenomenon [32,43], the value of the glass transition temperature depends on the cooling rate and is not a material constant. The state of the system in the glassy state is termed "metastable equilibrium" [44], "state of frozen structure" [30] or "frozen-in non-equilibrium state" [42] depending on the literature used.

The glass transition is visible in material properties such as the

- mechanical modulus or compliance,
- coefficient of thermal expansion,
- specific heat.

It also occurs on varying the frequency in a cyclic experiment, a fact which is often denoted "time–temperature" – or "frequency–temperature" – correspondence, respectively [45]. The described effects also occur as a result of electric excitations and lead to a frequency dependence of the dielectric response function which is similar to that of the specific heat (see Refs. [31,33]). In the glass-forming region, all material properties exhibit a pronounced dependence on both the frequency and the temperature at which the mechanical or the thermal excitation is applied with small changes in the input resulting in large changes in the output quantity [2,3,8,9,13,17,26]. While the component in-phase with the excitation, the storage component, changes from a higher to a lower value or vice versa, depending on the property, the out-of-phase or

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Nomenclature

t, ω	time and angular frequency
P_{DSC}	power absorbed by the sample
$\Delta m, \Delta V, \rho$	mass, volume and mass density of the sample
ψ, g, s, e	Helmholtz and Gibbs free energy, entropy and internal energy per unit mass
$\mathbf{T}, \mathbf{E}, \dot{\mathbf{T}}, \dot{\mathbf{E}}$	stress and strain tensor and their time derivatives
σ, ε	uniaxial stress and strain
$\vec{q}, r$	heat flux vector and volume-distributed heat supply per unit mass
θ, γ	thermodynamic temperature and rate of entropy production
ref	index of variables associated with the equilibrium reference state
$\vartheta, \hat{\vartheta}$	temperature perturbation and its amplitude
$\underset{\sim}{\delta}$	non-equilibrium perturbation of the internal variable vector
η, χ, τ	non-equilibrium perturbation of entropy, strain and stress
a, b, u, k, ν	scalar material parameters in the approximation of the Gibbs free energy
$\underset{\sim}{c}, \underset{\sim}{e}, \underset{\sim}{w}$	material parameter vectors in the approximation of the Gibbs free energy
$c_{p0}, c_{v0}, E_0, \kappa_0$	physical material parameters belonging to the glassy state
n	number of internal variables
$\underset{\approx}{d}, \underset{\approx}{A}$	material parameter matrices of dimension $n \times n$
$\hat{\underset{\sim}{\Delta}}_p, \hat{\underset{\sim}{\Delta}}_v, \hat{\underset{\sim}{\Delta}}_\tau, \hat{\underset{\sim}{\Delta}}_\chi$	transfer function vectors of the internal variables
$\hat{c}_p, \hat{c}_v$	complex specific heat at constant stress and strain
$\hat{J}, \hat{E}$	complex compliance and modulus
$\hat{\kappa}, \hat{\mu}$	complex coefficient of thermal expansion and thermal modulus
$\mathrm{div}\,(\cdot)$	divergence operator: $\mathrm{div}(\vec{q}) = \partial q_1/\partial x_1 + \partial q_2/\partial x_2 + \partial q_3/\partial x_3$
$\mathrm{grad}\,(\cdot)$	gradient operator: $\mathrm{grad}(\theta) = \left(\partial\theta/\partial x_1\right)\vec{e}_1 + \left(\partial\theta/\partial x_2\right)\vec{e}_2 + \left(\partial\theta/\partial x_3\right)\vec{e}_3$
$\alpha_k, \underset{\sim}{\alpha}$	scalar internal variable and column vector: $\underset{\sim}{\alpha} = (\alpha_1, \ldots, \alpha_n)^T$
$\underset{\sim}{f}, \underset{\sim}{\tilde{f}}$	column vector of the functions $\underset{\sim}{f} = (f_1, \ldots, f_n)^T$ and $\underset{\sim}{\tilde{f}} = (\tilde{f}_1, \ldots, \tilde{f}_n)^T$
$\underset{\approx}{1}, \underset{\approx}{X}^{-1}$	unit matrix of dimension $n \times n$, inverse of the $n \times n$ matrix $\underset{\approx}{X}$ with $\underset{\approx}{X}\underset{\approx}{X}^{-1} = \underset{\approx}{1}$
$\mathbf{X} \cdot \mathbf{Y}$	scalar product between two second order tensors: $\mathbf{X} \cdot \mathbf{Y} = \sum_{i,k=1}^{3} X_{ik} Y_{ik}$
$\vec{x} \cdot \vec{y}$	scalar product between two physical vectors: $\vec{x} \cdot \vec{y} = \sum_{i=1}^{3} x_i y_i$
$\underset{\sim}{x} \cdot \underset{\sim}{y}$	scalar product between two columns: $\underset{\sim}{x} \cdot \underset{\sim}{y} = \sum_{k=1}^{n} x_k y_k$
$\mathrm{Re}(z), \mathrm{Im}(z)$	real and imaginary parts of a complex number z

loss component runs through a maximum in the glass-transition region.

The mechanical, frequency-dependent, material behaviour can be investigated experimentally by prescribing a sinusoidal strain or stress history and measuring the modulus or compliance. The theory of linear viscoelasticity, see e.g. Tobolsky [6], has been successfully applied to model the observed phenomena whether it is discrete or continuous spectra, hence linear differential equations or convolution integrals, being used as depicted by Tschoegl [4] or Gross [5] or approaches from fractional calculus as used by Lion [7].

Mechanical tests in which the temperature is a prescribed function of time are uncommon and rare. Exceptions are static temperature-controlled tests to determine the coefficient of thermal expansion. Bauer et al. remarked in Ref. [9] "On the other hand, we do not know of an experimental report on the explicit frequency dependence of the thermal expansivity". In this article as well as in Ref. [10], the frequency dependence of the thermal expansion behaviour of polystyrene films was illustrated by them for the first time. As a result, the characteristic behaviour of the components of the complex coefficient of thermal expansion could be established: the storage component changes from a lower glassy value to a higher relaxed value as the temperature about which the perturbation is applied is increased while at the same time the loss component runs through a maximum.

Experimental investigations under continuously varying temperature excitations and constant stress (or pressure) are carried out to analyse the calorimetric material properties and to determine the heat capacity. Commonly used techniques are differential scanning calorimetry, known as DSC, and temperature-modulated differential scanning calorimetry, known as TMDSC. In this context, the reader is referred to the textbook by Höhne et al. [12]. In classical DSC, the temperature of the specimen changes with constant rate whereas in TMDSC a sinusoidal temperature oscillation with small amplitude is superimposed. The frequency dependence of the specific heat of glycerol, a well-known glass-forming substance, has originally been observed and physically interpreted by Christensen [14] or Birge and Nagel [26] and later by Minakov et al. [15] or Bentefour et al. [16], to name a few. For the representation and the interpretation of the frequency dependence of the specific heat in the context of irreversible thermodynamics, different approaches have been developed in the last decade (see e.g. Refs. [17–21]).

Christensen et al. [2] localized an essential problem if the specific heat $c_p(\omega)$ of a highly viscous liquid is measured using a thin specimen which is fixed on a substrate. As it is known from gases, the specific heat depends on the boundary conditions: if the volume is constant, the specific heat c_v is measured, and if the pressure is constant c_p is measured. According to Ref. [2], the oscillating temperature induces oscillating thermal strains when the pressure is constant. If, on the other hand, the volume is constant, the thermal strains are suppressed. This leads to thermal stresses which influence the specific heat. If the specific heat of a thin film of a highly viscous liquid is measured, neither the pressure nor the volume is constant in space and time. In order to clarify this aspect, it is indispensable to investigate the mechanical material properties in the neighbourhood of the glass transition as well. Christensen et al. have shown in [2], that Birge and Nagel [26], measured the so-called longitudinal specific heat.

This short literature review has shown that glass-forming materials exhibit frequency-dependent effects which can be observed in properties such as the compliance, the coefficient of thermal expansion and the specific heat. It has been known for a long time that the different frequency-dependent response functions are not independent from each other (see Refs. [30,32,34,38]). But despite this fact, closed-form expressions for these quantities, their couplings and their dependence on material parameters have not been derived and interpreted in a single consistent model so far.

Inspired by the works published in Refs. [2,29,30], the other literature cited above and earlier works of our group [20,24,25], it is the objective of this essay to provide a single constitutive approach on the basis of thermodynamics with internal state variables from which explicit relations for the frequency-dependent specific heat at constant stress or strain, the thermal expansion behaviour and the dynamic mechanical response functions can be derived.

Based on the fundamentals provided in the following chapter, the model is formulated for one-dimensional states of stress and strain. In the neighbourhood of a state of thermodynamic equilibrium as a reference state, the specific Gibbs free energy is approximated using a Taylor series up to second order terms depending on stress, temperature and a set of internal variables. This approach was motivated by the article of Lesikar and Moynihan [30]. With the help of the Legendre transform and after applying the tools provided by the theory of thermodynamics, closed-form relations for the mentioned material properties are established. Also different forms of the Prigogine–Defay ratio can be obtained from the model presented.

Before getting into the modelling part, a short discussion is needed, since several conceptions regarding the introduction of additional state variables are used in literature to describe glass-forming materials. From the mathematical point of view, internal variables [4,20,23,28], configurational or fictive temperatures [37,39] or order parameters [30,32,35,39,41] are introduced for one and the same reason: if a material exhibits a history-dependent behaviour, the current values of stress or strain and temperature or entropy are not sufficient to characterise its current state. From the point of view of phenomenological material modelling, fictive or configurational temperatures and order parameters can be interpreted as internal variables with special physical meanings. In models of viscoelasticity, for example, which are formulated using Maxwell chains, the definition of the internal variables is not unique: both the inelastic strains of the dashpots or the stresses of the Maxwell elements can be taken as internal variables. It is also possible, to eliminate the internal variables and to represent the current stress as a linear functional of the strain history. A detailed study regarding the number of internal variables which is necessary to model the glass transition leads to the Prigogine–Defay condition, which is an inequality between the temperature- or frequency-induced changes in specific heat, thermal expansion coefficient and compressibility. The reader who is interested in this field is referred to refs. [30,32,34–36,38]. In the current paper, the discussion whether one or more internal variables are necessary to model the dynamic material behaviour in the vicinity of the glass transition is not conducted. It should be mentioned, however, that there is an ongoing discussion on the number of variables which is required to describe the dynamics of glass-forming substances [36,41]. Since the microstructure of glass-forming materials does not change at the glass transition (see Ref. [46]), the internal variables introduced in this paper have no structural counterpart: they are introduced to describe the history-dependent material behaviour.

2. Fundamentals

In order to formulate the constitutive model, some basics are introduced first. For more details the reader is referred to the textbooks of Haupt [22] or Maugin [23]. The thermodynamic potentials used in this paper are the specific Gibbs and Helmholtz free energy. The specific Helmholtz free energy per unit mass is defined as

$$\psi = e - \theta s. \tag{2.1}$$

The quantity s is the specific entropy per unit mass, θ the thermodynamic temperature and e the specific internal energy per unit mass. The specific Gibbs free energy is defined as

$$g = \psi - \frac{1}{\rho}\mathbf{T}\cdot\mathbf{E}. \tag{2.2}$$

$\mathbf{T}$ is the stress tensor, $\mathbf{E}$ the infinitesimal strain tensor and ρ the mass density. As shown in Ref. [20], the corresponding formulations of the local balance equation of energy, or the first law of thermodynamics, read as

$$\rho\dot{\psi} = \mathbf{T}\cdot\dot{\mathbf{E}} - \rho\left(\theta\dot{s} + s\dot{\theta}\right) - \operatorname{div}\left(\vec{q}\right) + \rho r, \tag{2.3}$$

$$\rho\dot{g} = -\mathbf{E}\cdot\dot{\mathbf{T}} - \rho\left(\theta\dot{s} + s\dot{\theta}\right) - \operatorname{div}\left(\vec{q}\right) + \rho r. \tag{2.4}$$

The vector $\vec{q}$ is the heat flux and r the heat supply per unit mass. The related formulations of the Clausius–Duhem inequality, or the second law of thermodynamics, can be written as

$$\rho\theta\gamma = -\rho\dot{\psi} + \mathbf{T}\cdot\dot{\mathbf{E}} - \rho s\dot{\theta} - \frac{\vec{q}\cdot\operatorname{grad}(\theta)}{\theta} \geq 0, \tag{2.5}$$

$$\rho\theta\gamma = -\rho\dot{g} - \mathbf{E}\cdot\dot{\mathbf{T}} - \rho s\dot{\theta} - \frac{\vec{q}\cdot\operatorname{grad}(\theta)}{\theta} \geq 0. \tag{2.6}$$

The Clausius–Duhem inequality states that the specific entropy production per unit time γ always has to be non-negative. This statement has to be satisfied by any constitutive model for arbitrary thermomechanical processes.

If the Helmholtz free energy ψ is taken as thermodynamic potential the rates of strain and temperature occur in (2.5); if the Gibbs free energy g is taken as potential, the rates of stress and temperature occur in the corresponding form (2.6) of the Clausius–Duhem inequality. This structure motivates the following sets of canonical independent variables of ψ and g:

$$\psi = \psi\left(\mathbf{E}, \theta, \underline{\alpha}\right) \tag{2.7}$$

$$g = g\left(\mathbf{T}, \theta, \underline{\alpha}\right) \tag{2.8}$$

The internal state variables

$$\underline{\alpha} = (\alpha_1, \ldots, \alpha_n)^T \tag{2.9}$$

are introduced to consider the dependence of the material behaviour on the history of strain or stress and temperature. The evolution of the internal variables is modelled by a system of differential equations depending on θ and $\mathbf{E}$ or, alternatively, on θ and $\mathbf{T}$:

$$\dot{\underline{\alpha}}(t) = \underline{\tilde{f}}\left(\mathbf{E}, \theta, \underline{\alpha}\right) \quad \text{with} \quad \underline{\tilde{f}} = \left(\tilde{f}_1, \ldots, \tilde{f}_n\right)^T \tag{2.10}$$

$$\dot{\underline{\alpha}}(t) = \underline{f}\left(\mathbf{T}, \theta, \underline{\alpha}\right) \quad \text{with} \quad \underline{f} = (f_1, \ldots, f_n)^T \tag{2.11}$$

The column vectors of the partial derivatives

$$\frac{\partial\psi}{\partial\underline{\alpha}} = \left(\frac{\partial\psi}{\partial\alpha_1}, \ldots, \frac{\partial\psi}{\partial\alpha_n}\right)^T \quad \text{and} \quad \frac{\partial g}{\partial\underline{\alpha}} = \left(\frac{\partial g}{\partial\alpha_1}, \ldots, \frac{\partial g}{\partial\alpha_n}\right)^T \tag{2.12}$$

in combination with the scalar products

$$\frac{\partial\psi}{\partial\underline{\alpha}}\cdot\dot{\underline{\alpha}} = \sum_{k=1}^{n}\frac{\partial\psi}{\partial\alpha_k}\dot{\alpha}_k \quad \text{and} \quad \frac{\partial g}{\partial\underline{\alpha}}\cdot\dot{\underline{\alpha}} = \sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k \tag{2.13}$$

are introduced to allow for a compact notation. For the considerations in the next chapters, the formulations of the equation of heat conduction with the Gibbs and Helmholtz free energies are needed (the details of this calculation are sketched in Appendix A):

$$-\rho\theta\frac{\partial^2\psi}{\partial\theta^2}\dot{\theta} + \rho\left(\frac{\partial\psi}{\partial\underline{\alpha}} - \theta\frac{\partial^2\psi}{\partial\theta\partial\underline{\alpha}}\right)\cdot\underline{\tilde{f}} = \rho\theta\frac{\partial^2\psi}{\partial\theta\partial\mathbf{E}}\cdot\dot{\mathbf{E}} - \operatorname{div}(\vec{q}) + \rho r \tag{2.14}$$

$$-\rho\theta\frac{\partial^2 g}{\partial\theta^2}\dot{\theta} + \rho\left(\frac{\partial g}{\partial\underline{\alpha}} - \theta\frac{\partial^2 g}{\partial\theta\partial\underline{\alpha}}\right)\cdot\underline{f} = \rho\theta\frac{\partial^2 g}{\partial\theta\partial\mathbf{T}}\cdot\dot{\mathbf{T}} - \operatorname{div}(\vec{q}) + \rho r \tag{2.15}$$

When studying thermomechanical processes at constant strain, the first term on the right-hand side of (2.14) vanishes and the formulation of the constitutive model with the Helmholtz free energy is favourable. But if the stress is constant the equation of heat conduction in the form of (2.15) is more useful.

3. Constitutive model

The constitutive model to be developed is formulated to describe the material behaviour in the neighbourhood of a state thermodynamic equilibrium as a reference state. The reference state is defined by constant values of all external and internal state variables and its neighbourhood by sufficiently small changes in these quantities. A similar concept has been applied some years earlier in Ref. [30] in order to model dielectric relaxation effects in glasses.

For the following considerations, two equivalent formulations of the constitutive model are needed: the primary formulation is based on the specific Gibbs free energy as thermodynamic potential and the secondary formulation on the Helmholtz free energy. To sketch the main ideas and to reduce the mathematical formalism to a minimum, a one-dimensional state of stress is assumed such that the three-dimensional stress tensor $\mathbf{T} = \sigma \vec{e}_1 \otimes \vec{e}_1$ can be replaced by the scalar stress σ. The strain in the corresponding direction is denoted as ε and the lateral strains as ε_2 and ε_3 such that $\mathbf{E} = \varepsilon \vec{e}_1 \otimes \vec{e}_1 + \varepsilon_2 \vec{e}_2 \otimes \vec{e}_2 + \varepsilon_3 \vec{e}_3 \otimes \vec{e}_3$ is the three-dimensional strain tensor. As a consequence, $\mathbf{T} \cdot \mathbf{E} = \sigma\varepsilon$ holds. Under these assumptions, from (2.7), (2.8) and (A.5)–(A.8) in Appendix A the relations which are summarized in Table 1 are obtained.

The state of the material in the equilibrium reference state is characterised by constant values of temperature θ_{ref}, strain ε_{ref}, stress σ_{ref}, entropy s_{ref}, Gibbs free energy g_{ref} and Helmholtz free energy ψ_{ref} as well as by the constant internal variable vector $\underline{\alpha}_{\text{ref}}$. The Gibbs and Helmholtz free energies belonging to this state are given by the expressions

$$g_{\text{ref}} = g(\sigma_{\text{ref}}, \theta_{\text{ref}}, \underline{\alpha}_{\text{ref}}), \tag{3.1}$$

$$\psi_{\text{ref}} = \psi(\varepsilon_{\text{ref}}, \theta_{\text{ref}}, \underline{\alpha}_{\text{ref}}). \tag{3.2}$$

The rate of change in the internal variables vanishes in the equilibrium and the resulting equations can be used to calculate $\underline{\alpha}_{\text{ref}}$ (cf. Ref. [30]):

$$\underline{0} = \underline{f}(\sigma_{\text{ref}}, \theta_{\text{ref}}, \underline{\alpha}_{\text{ref}}) \Leftrightarrow \underline{\alpha}_{\text{ref}} = \underline{\varphi}(\sigma_{\text{ref}}, \theta_{\text{ref}}) \tag{3.3}$$

$$\underline{0} = \underline{\tilde{f}}(\varepsilon_{\text{ref}}, \theta_{\text{ref}}, \underline{\alpha}_{\text{ref}}) \Leftrightarrow \underline{\alpha}_{\text{ref}} = \underline{\tilde{\varphi}}(\varepsilon_{\text{ref}}, \theta_{\text{ref}}) \tag{3.4}$$

To model the non-equilibrium behaviour of the material, a set of time-dependent perturbation functions τ, ϑ, η, χ and $\underline{\delta}$ is introduced such that the current values of stress, temperature, entropy, strain and internal variables can be expressed as

$$\sigma(t) = \sigma_{\text{ref}} + \tau(t), \tag{3.5}$$

$$\theta(t) = \theta_{\text{ref}} + \vartheta(t), \tag{3.6}$$

$$s(t) = s_{\text{ref}} + \eta(t), \tag{3.7}$$

$$\varepsilon(t) = \varepsilon_{\text{ref}} + \chi(t), \tag{3.8}$$

$$\underline{\alpha}(t) = \underline{\alpha}_{\text{ref}} + \underline{\delta}(t). \tag{3.9}$$

The perturbation functions are assumed to vanish in the reference state. It is also assumed that they are sufficiently small such that a quadratic approximation of the Gibbs free energy can be used to model the physical phenomena of interest.

3.1. Formulation with the Gibbs free energy

To represent the non-equilibrium behaviour of the Gibbs free energy Ref. [20] is followed and the approximation used there is extended by the stress perturbation and its couplings with the changes in the temperature and the internal variables:

$$\begin{aligned} g(\sigma, \theta, \underline{\alpha}) = {} & g_{\text{ref}} + a\vartheta + \frac{b}{2}\vartheta^2 + \underline{c} \cdot \underline{\delta} + \frac{1}{2}(\underline{\underline{d}}\,\underline{\delta}) \cdot \underline{\delta} + \underline{e} \cdot \underline{\delta}\vartheta + u\tau \\ & + \frac{k}{2}\tau^2 + v\tau\vartheta + \underline{w} \cdot \underline{\delta}\tau \end{aligned} \tag{3.10}$$

The quantities $\underline{c}$, $\underline{e}$ and $\underline{w}$ are column vectors of dimension n containing material constants; g_{ref}, a, b, u, k, v are scalar material parameters. The $n \times n$ matrix $\underline{\underline{d}}$ contains material constants and is assumed to be positive definite, symmetric and invertible, i.e. $\underline{x} \cdot \left(\underline{\underline{d}}\,\underline{x}\right) > 0$ as well as $\underline{x} \cdot \left(\underline{\underline{d}}\,\underline{\underline{d}}^{-1}\underline{\underline{d}}\,\underline{x}\right) = \left(\underline{\underline{d}}\,\underline{x}\right) \cdot \underline{\underline{d}}^{-1} \left(\underline{\underline{d}}\,\underline{x}\right) > 0$ holds for arbitrary vectors $\underline{x} \neq \underline{0}$.

Evaluating the potential relations for the strain and the specific entropy on the right-hand side of Table 1 and calculating the entropy production leads to the following expressions:

$$\varepsilon_{\text{ref}} + \chi(\tau, \vartheta, \underline{\delta}) = -\rho\frac{\partial g}{\partial \tau} = -\rho(u + k\tau + v\vartheta + \underline{w} \cdot \underline{\delta}) \tag{3.11}$$

$$s_{\text{ref}} + \eta(\tau, \vartheta, \underline{\delta}) = -\frac{\partial g}{\partial \vartheta} = -(a + b\vartheta + \underline{e} \cdot \underline{\delta} + v\tau) \tag{3.12}$$

$$-\frac{\partial g}{\partial \underline{\delta}} \cdot \dot{\underline{\delta}} = -(\underline{c} + \underline{\underline{d}}\,\underline{\delta} + \underline{e}\vartheta + \underline{w}\tau) \cdot \dot{\underline{\delta}} \geq 0 \tag{3.13}$$

The requirement for a non-negative entropy production (see Table 1) motivates the following system of differential equations for the internal variables

$$\dot{\underline{\delta}} = -\underline{\underline{A}}\left(\underline{c} + \underline{\underline{d}}\,\underline{\delta} + \underline{e}\vartheta + \underline{w}\tau\right), \quad \underline{\delta}(0) = \underline{0}, \tag{3.14}$$

where the matrix $\underline{\underline{A}}$ is symmetric and positive definite and contains additional material parameters. For the initial conditions at time $t = 0$, $\underline{\delta}(0) = \underline{0}$ is assumed. The evaluation of (3.11), (3.12) and (3.14) in the equilibrium leads to

$$\varepsilon_{\text{ref}} = -\rho u, \tag{3.15}$$

$$s_{\text{ref}} = -a, \tag{3.16}$$

$$\dot{\underline{\delta}}(0, 0, \underline{0}) = -\underline{\underline{A}}\,\underline{c}. \tag{3.17}$$

To avoid that the internal variables evolve in the equilibrium $\underline{c} = \underline{0}$ must hold. Assuming an infinitely fast stress-controlled process under isothermal conditions such that $\tau(t) \neq 0$ and $\vartheta(t) \equiv 0$, (3.14) leads to $\underline{\delta}(t) = \underline{0}$. Thus, the internal variables remain frozen under infinitely fast changes in stress. Taking $\underline{\delta}(t) = \underline{0}$ in combination with $u = 0$ and (3.11) into account a linear elastic relation for the change in the strain is obtained:

$$\chi = -\rho k\tau =: \frac{1}{E_0}\tau \tag{3.18}$$

The constant $E_0 = -1/(\rho k)$ is the glassy or spontaneous elastic modulus. If an infinitely fast temperature-controlled stress-free process is prescribed, i.e. $\tau(t) \equiv 0$ and $\vartheta(t) \neq 0$, (3.14) also leads to $\underline{\delta}(t) = \underline{0}$. Taking this in combination with $u = 0$ and (3.11) into account a linear relation between the changes in temperature and strain is obtained:

$$\chi = -\rho v\vartheta =: \kappa_0\vartheta. \tag{3.19}$$

The parameter $\kappa_0 = -\rho v$ can be interpreted as the glassy or spontaneous coefficient of thermal expansion.

With the definition (A.21) in Appendix A the specific heat at constant stress can be calculated:

$$c_p\left(\tau, \vartheta, \underline{\delta}\right) = -\left(\theta_{\text{ref}} + \vartheta\right)\frac{\partial^2 g}{\partial \vartheta^2} = -\left(\theta_{\text{ref}} + \vartheta\right) b \tag{3.20}$$

Table 1
Thermodynamic relations for the one-dimensional constitutive model.

Thermodynamic potential	$\psi = \psi\left(\varepsilon, \theta, \underline{\alpha}\right)$	$g = g\left(\sigma, \theta, \underline{\alpha}\right)$
Stress or strain	$\sigma\left(\varepsilon, \theta, \underline{\alpha}\right) = \rho\partial\psi/\partial\varepsilon$	$\varepsilon\left(\sigma, \theta, \underline{\alpha}\right) = -\rho\partial g/\partial\sigma$
Specific entropy	$s(\varepsilon, \theta, \underline{\alpha}) = -\partial\psi/\partial\theta$	$s(\sigma, \theta, \underline{\alpha}) = -\partial g/\partial\theta$
Evolution of the internal variables	$\dot{\underline{\alpha}}(t) = \underline{\tilde{f}}(\varepsilon, \theta, \underline{\alpha})$	$\dot{\underline{\alpha}}(t) = \underline{f}(\sigma, \theta, \underline{\alpha})$
Entropy production of internal variables	$\rho\theta\gamma = -\rho\partial\psi/\partial\underline{\alpha} \cdot \underline{\tilde{f}} \geq 0$	$\rho\theta\gamma = -\rho\partial g/\partial\underline{\alpha} \cdot \underline{f} \geq 0$

Evaluating (3.20) in the glassy state, i.e. for $\vartheta = 0$, $|\dot{\vartheta}| \to \infty$, $\underline{\delta} = \underline{0}$, the constant

$$c_{p0} := c_p(0, 0, \underline{0}) = -\theta_0 b \tag{3.21}$$

is defined. It is the specific heat in the glassy state.

With the material parameters defined so far, the basic equations defining the constitutive model on the basis of the Gibbs free energy can be written as follows:

$$\text{Gibbs free energy}: g = g_{\text{ref}} - s_{\text{ref}}\vartheta - \frac{c_{p0}}{2\theta_{\text{ref}}}\vartheta^2 + \frac{1}{2}\left(\underline{\underline{d}}\underline{\delta}\right) \cdot \underline{\delta} + \underline{e} \cdot \underline{\delta}\vartheta - \frac{\varepsilon_{\text{ref}}}{\rho}\tau - \frac{1}{2\rho E_0}\tau^2 - \frac{\kappa_0}{\rho}\tau\vartheta + \underline{w} \cdot \underline{\delta}\tau \tag{3.22}$$

$$\text{Strain}: \chi = \frac{1}{E_0}\tau + \kappa_0\vartheta - \rho\underline{w} \cdot \underline{\delta} \tag{3.23}$$

$$\text{Entropy}: \eta = \frac{c_{p0}}{\theta_{\text{ref}}}\vartheta - \underline{e} \cdot \underline{\delta} + \frac{\kappa_0}{\rho}\tau \tag{3.24}$$

$$\text{Internal variables}: \dot{\underline{\delta}} = -\underline{\underline{A}}\left(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta + \underline{w}\tau\right) \tag{3.25}$$

In this theory, the changes in strain and entropy as well as the rates of the internal variables are linear functions of the changes in the independent state variables. It is profitable when the stress is used as mechanical state variable. If not the stress but the strain is used as independent mechanical state variable, the formulation of the model with the Helmholtz free energy is more profitable. The corresponding formulation is derived in Appendix B.

4. Frequency-dependent specific heat at constant stress and constant strain

For the calculation of the frequency-dependent specific heat at constant stress $\hat{c}_p(\omega)$ and at constant strain $\hat{c}_v(\omega)$ the balance equation of energy in the form of (2.14) and (2.15) is considered. In the case of $\hat{c}_p(\omega)$ the Gibbs free energy is the appropriate potential while in the case of $\hat{c}_v(\omega)$ the Helmholtz free energy is suitable. The function $\hat{c}_v(\omega)$ can also be calculated on the basis of the Gibbs free energy, but the calculation is more costly since the changes in stress at constant strain have to be considered in the balance equation of energy (2.15).

Assuming the stress or the strain to be constant, considering (3.6) and setting the volume-distributed heat supply r to zero, the following relations are obtained from (2.14) and (2.15):

$$\text{Constant stress}: -(\theta_{\text{ref}} + \vartheta)\frac{\partial^2 g}{\partial\vartheta^2}\dot{\vartheta} + \left(\frac{\partial g}{\partial\underline{\delta}} - (\theta_{\text{ref}} + \vartheta)\frac{\partial^2 g}{\partial\vartheta\partial\underline{\delta}}\right) \cdot \dot{\underline{\delta}} = -\frac{1}{\rho}\text{div}(\vec{q}) \tag{4.1}$$

$$\text{Constant strain}: -(\theta_{\text{ref}} + \vartheta)\frac{\partial^2 \psi}{\partial\vartheta^2}\dot{\vartheta} + \left(\frac{\partial \psi}{\partial\underline{\delta}} - (\theta_{\text{ref}} + \vartheta)\frac{\partial^2 \psi}{\partial\vartheta\partial\underline{\delta}}\right) \cdot \dot{\underline{\delta}} = -\frac{1}{\rho}\text{div}(\vec{q}) \tag{4.2}$$

In Appendix C, relations (4.1) and (4.2) are evaluated and reformulated with regard to the constitutive assumptions (3.22)–(3.25), or (B.7)–(B.11), and prescribed temperature processes. If the heat power per unit mass which is absorbed or emitted by the specimen of mass Δm is denoted as $P_{\text{DSC}}(t)$, the following results are obtained:

$$\text{Constant stress}: c_{p0}\dot{\vartheta} + \theta_{\text{ref}}\,\underline{e} \cdot \left(\underline{\underline{A}}\left(\underline{e}\vartheta + \underline{\underline{d}}\underline{\delta}\right)\right) + c_{p0}\frac{\vartheta}{\theta_{\text{ref}}}\dot{\vartheta} - \underline{\delta} \cdot \left(\underline{\underline{dA}}\left(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta\right)\right) = \frac{P_{\text{DSC}}(t)}{\Delta m} \tag{4.3}$$

$$\text{Constant strain}: c_{v0}\dot{\vartheta} + \theta_{\text{ref}}\,\underline{\tilde{e}} \cdot \left(\underline{\underline{A}}\left(\underline{\tilde{e}}\vartheta + \underline{\underline{\tilde{d}}}\underline{\delta}\right)\right) + c_{v0}\frac{\vartheta}{\theta_{\text{ref}}}\dot{\vartheta} - \underline{\delta} \cdot \left(\underline{\underline{\tilde{d}A}}\left(\underline{\underline{\tilde{d}}}\underline{\delta} + \underline{\tilde{e}}\vartheta\right)\right) = \frac{P_{\text{DSC}}(t)}{\Delta m} \tag{4.4}$$

If the temperature change $\vartheta(t)$ is a prescribed function of time, (4.3) and (4.4) can be used to calculate the calorimetric response $P_{\text{DSC}}(t)$ under constant stress or strain conditions. To compute the frequency-dependent specific heat at constant stress or strain, a harmonic temperature change with angular frequency ω and amplitude $\hat{\vartheta}$ is prescribed:

$$\vartheta(t) = \hat{\vartheta}e^{i\omega t} \tag{4.5}$$

For this process, the linear differential Eqs. (3.25) and (B.8) can be solved for $\tau = 0$ and $\chi = 0$, respectively, in closed form. Their stationary solutions are expressed as

$$\underline{\delta}_p(t) = \hat{\underline{\Delta}}_p(\omega)\hat{\vartheta}e^{i\omega t}, \tag{4.6}$$

$$\underline{\delta}_v(t) = \hat{\underline{\Delta}}_v(\omega)\hat{\vartheta}e^{i\omega t}. \tag{4.7}$$

The vectors $\hat{\underline{\Delta}}_v(\omega)$ and $\hat{\underline{\Delta}}_p(\omega)$ are the transfer functions of the internal variables for $\chi = 0$ and for $\tau = 0$. Considering (4.5), (3.25) and (B.8), they can be calculated as

$$\hat{\underline{\Delta}}_p(\omega) = -\left(i\omega\underline{\underline{1}} + \underline{\underline{Ad}}\right)^{-1}\underline{\underline{Ae}}, \tag{4.8}$$

$$\hat{\underline{\Delta}}_v(\omega) = -\left(i\omega\underline{\underline{1}} + \underline{\underline{A\tilde{d}}}\right)^{-1}\underline{\underline{A\tilde{e}}}. \tag{4.9}$$

Inserting (4.5) in combination with (4.6), (4.7) and the transfer functions (4.8), (4.9) into (4.3) and (4.4) and rearranging the terms leads to:

$$\text{Constant stress}: \left(c_{p0} - \theta_{\text{ref}}\,\underline{e} \cdot \hat{\underline{\Delta}}_p(\omega)\right)i\omega\hat{\vartheta}e^{i\omega t} + i\omega\left(\frac{c_{p0}}{\theta_{\text{ref}}} + \hat{\underline{\Delta}}_p(\omega) \cdot \underline{\underline{d}}\hat{\underline{\Delta}}_p(\omega)\right)\hat{\vartheta}^2 e^{2i\omega t} = \frac{P_{\text{DSC}}}{\Delta m} \tag{4.10}$$

$$\text{Constant strain}: \left(c_{v0} - \theta_{\text{ref}}\,\underline{\tilde{e}} \cdot \hat{\underline{\Delta}}_v(\omega)\right)i\omega\hat{\vartheta}e^{i\omega t} + i\omega\left(\frac{c_{v0}}{\theta_{\text{ref}}} + \hat{\underline{\Delta}}_v(\omega) \cdot \underline{\underline{\tilde{d}}}\hat{\underline{\Delta}}_v(\omega)\right)\hat{\vartheta}^2 e^{2i\omega t} = \frac{P_{\text{DSC}}}{\Delta m} \tag{4.11}$$

As can be seen, there are two frequencies in the calorimetric responses (4.10) and (4.11): one term oscillates with ω and the other with 2ω. The 2ω-term is small because it is multiplied with

$\hat{\vartheta}^2$ [20]. Since the factor $i\omega\hat{\vartheta}e^{i\omega t}$ is the temperature rate, its coefficients can be interpreted as frequency-dependent specific heat at constant stress and or strain, respectively:

$$\hat{c}_p(\omega) = c_{p0} - \theta_{\text{ref}}\ \underline{e} \cdot \hat{\underline{\Delta}}_p(\omega) \tag{4.12}$$

$$\hat{c}_v(\omega) = c_{v0} - \theta_{\text{ref}}\ \underline{\tilde{e}} \cdot \hat{\underline{\Delta}}_v(\omega) \tag{4.13}$$

Taking (4.8) and (4.9) as well as (B.9), (B.10) and (B.11) in Appendix B into account, the explicit forms of the frequency dependent specific heat read as:

$$\hat{c}_p(\omega) = c_{p0} + \theta_{\text{ref}}\ \underline{e} \cdot \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1} \underline{\underline{A}}\,\underline{e} \tag{4.14}$$

$$\begin{aligned}\hat{c}_v(\omega) = c_{p0} - \frac{\theta_{\text{ref}} E_0 \kappa_0^2}{\rho} + \theta_{\text{ref}}\left(\underline{e} - E_0\kappa_0\underline{w}\right)\\ \cdot\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\left(\underline{\underline{d}} + \rho E_0 \underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\left(\underline{e} - E_0\kappa_0\underline{w}\right)\end{aligned} \tag{4.15}$$

The expression (4.15) of the frequency-dependent specific heat at constant strain has the same structure as (4.14) which is the frequency-dependent specific heat at constant stress. It is influenced, however, by additional material parameters: the spontaneous elastic modulus E_0, the spontaneous coefficient of thermal expansion κ_0, the density ρ and the parameter vector $\underline{w}$ which describes the couplings between the stress and the internal variables.

5. Frequency-dependent, temperature-induced stresses and strains

In order to calculate the frequency-dependent thermal expansion behaviour, a harmonic temperature excitation in the form of (4.5) is assumed and the change in stress is set to zero, i.e. $\tau = 0$. For these conditions, the constitutive Eqs. (3.23) and (3.25) are solved:

$$\chi = \kappa_0\vartheta - \rho\underline{w}\cdot\underline{\delta} \tag{5.1}$$

$$\dot{\underline{\delta}} = -\underline{\underline{A}}\left(\underline{\underline{d}}\,\underline{\delta} + \underline{e}\vartheta\right) \tag{5.2}$$

In this case, the temperature-induced strain can be represented as

$$\chi(t) = \hat{\chi}(\omega)\,e^{i\omega t}. \tag{5.3}$$

The function $\hat{\chi}(\omega)$ is the complex strain amplitude and the frequency-dependent coefficient of thermal expansion is defined by the ratio

$$\hat{\kappa}(\omega) = \frac{\hat{\chi}(\omega)}{\hat{\vartheta}}. \tag{5.4}$$

The harmonic solution of the evolution Eq. (5.2) is given by (4.6). A simple calculation leads to

$$\hat{\kappa}(\omega) = \kappa_0 - \rho\underline{w}\cdot\hat{\underline{\Delta}}_p(\omega). \tag{5.5}$$

Inserting the transfer function (4.8) of the internal variables the following relation for the frequency-dependent coefficient of thermal expansion is obtained:

$$\hat{\kappa}(\omega) = \kappa_0 + \rho\underline{w}\cdot\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{e} \tag{5.6}$$

The parameter vector $\underline{w}$ describes the coupling between the stress and the internal variables and the vector $\underline{e}$ those between the temperature and the internal variables. If one of them is zero, the coefficient of thermal expansion is frequency-independent.

For the computation of the frequency-dependent stress response under constant strain, the temperature excitation (4.5) is prescribed, the change in strain is set to zero, and the equations (B.3) and (B.6) in Appendix B yielding

$$\tau = E_0\left(-\kappa_0\vartheta + \rho\underline{w}\cdot\underline{\delta}\right) \tag{5.7}$$

$$\dot{\underline{\delta}} = -\underline{\underline{A}}\left(\left(\underline{\underline{d}} + \rho E_0\underline{w}\otimes\underline{w}\right)\underline{\delta} + \left(\underline{e} - E_0\kappa_0\underline{w}\right)\vartheta\right) \tag{5.8}$$

are solved. The temperature-induced stress response has the functional form

$$\tau(t) = \hat{\tau}(\omega)\,e^{i\omega t}, \tag{5.9}$$

where $\hat{\tau}(\omega)$ is the stress amplitude. The frequency-dependent thermal modulus is defined as

$$\hat{\mu}(\omega) = \frac{\hat{\tau}(\omega)}{\hat{\vartheta}}. \tag{5.10}$$

The solution of the evolution Eq. (5.8) is given by (4.7) in combination with (4.9). A short calculation leads to

$$\hat{\mu}(\omega) = E_0\left(-\kappa_0 + \rho\underline{w}\cdot\hat{\underline{\Delta}}_v(\omega)\right). \tag{5.11}$$

Taking the expression of the transfer function (4.9) of the internal variables into account, the following result for the thermal modulus is obtained:

$$\hat{\mu}(\omega) = -E_0\left(\kappa_0 + \rho\underline{w}\cdot\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\left(\underline{\underline{d}} + \rho E_0\underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\left(\underline{e} - E_0\kappa_0\underline{w}\right)\right) \tag{5.12}$$

As it can be seen, this coefficient is frequency-independent if the parameter vector $\underline{w}$ is zero, i.e. if there is no coupling between the mechanical state variables and the internal variables.

6. Frequency-dependent mechanical material behaviour

Now, the isothermal mechanical behaviour for harmonic stress- and strain-controlled loadings is computed. In the case of a stress-controlled loading, an excitation with angular frequency ω and stress amplitude $\hat{\tau}$ is applied:

$$\tau(t) = \hat{\tau}e^{i\omega t} \tag{6.1}$$

The corresponding equations resulting from (3.23) and (3.25) read as

$$\chi = \frac{1}{E_0}\tau - \rho\underline{w}\cdot\underline{\delta}, \tag{6.2}$$

$$\dot{\underline{\delta}} = -\underline{\underline{A}}\left(\underline{\underline{d}}\,\underline{\delta} + \underline{w}\tau\right). \tag{6.3}$$

Since these equations are linear, their stationary responses can be represented as

$$\chi(t) = \hat{\chi}(\omega)e^{i\omega t}, \tag{6.4}$$

$$\underline{\delta}_\tau(t) = \hat{\underline{\Delta}}_\tau(\omega)\hat{\tau}e^{i\omega t}. \tag{6.5}$$

Inserting (6.1) and (6.5) into (6.3), the following expression for the transfer function of the internal variables under stress control is obtained:

$$\hat{\underline{\Delta}}_\tau(\omega) = -\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{w} \tag{6.6}$$

This outcome in combination with relation (6.2) leads to the intermediate result

$$\hat{\chi}(\omega) = \left(\frac{1}{E_0} - \rho\underline{w}\cdot\underline{\Delta}_\tau(\omega)\right)\hat{\tau}. \tag{6.7}$$

Considering the definition of the frequency-dependent complex compliance

$$\hat{J}(\omega) = \frac{\hat{\chi}(\omega)}{\hat{\tau}}, \tag{6.8}$$

the following expression applies:

$$\hat{J}(\omega) = \frac{1}{E_0} + \rho\underline{w} \cdot \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{w} \tag{6.9}$$

As can be noticed, the mathematical structure of the compliance $\hat{J}(\omega)$ is similar to that of the frequency-dependent specific heat (4.14) under constant stress.

In order to calculate the complex modulus

$$\hat{E}(\omega) = \frac{\hat{\tau}(\omega)}{\hat{\chi}} \tag{6.10}$$

under isothermal strain-controlled conditions, $\vartheta = 0$ is set and a sinusoidal strain excitation with constant amplitude and frequency is prescribed:

$$\chi(t) = \hat{\chi}e^{i\omega t} \tag{6.11}$$

The expressions determining the stress response $\tau(t) = \hat{\tau}(\omega)e^{i\omega t}$ result from (B.3) and (B.6):

$$\tau = E_0\left(\chi + \rho\underline{w} \cdot \underline{\delta}\right) \tag{6.12}$$

$$\dot{\underline{\delta}} = -\underline{\underline{A}}\left(\left(\underline{\underline{d}} + \rho E_0\underline{w} \otimes \underline{w}\right)\underline{\delta} + E_0\underline{w}\chi\right) \tag{6.13}$$

Postulating the relation

$$\underline{\delta}_\chi(t) = \hat{\underline{\Delta}}_\chi(\omega)\hat{\chi}e^{i\omega t} \tag{6.14}$$

for the stationary behaviour of the internal variables under strain control and taking (6.13) into account, the following relation for the transfer function is obtained:

$$\hat{\underline{\Delta}}_\chi(\omega) = -E_0\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\left(\underline{\underline{d}} + \rho E_0\underline{w} \otimes \underline{w}\right)\right)^{-1}\underline{\underline{A}}\,\underline{w} \tag{6.15}$$

This result in combination with (6.12) leads to the stress amplitude

$$\hat{\tau}(\omega) = E_0\left(1 + \rho\underline{w} \cdot \underline{\Delta}_\chi(\omega)\right)\hat{\chi} \tag{6.16}$$

and with the definition (6.10) to the following relation for the complex modulus:

$$\hat{E}(\omega) = E_0\left(1 - \rho E_0\underline{w} \cdot \left(\left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\left(\underline{\underline{d}} + \rho E_0\underline{w} \otimes \underline{w}\right)\right)^{-1}\underline{\underline{A}}\,\underline{w}\right)\right) \tag{6.17}$$

It is frequency-independent if the parameter vector $\underline{w}$ is zero, i.e. if no couplings between the internal variables and the stress exist.

7. Discussion

At this stage, the main consequences of the presented constitutive approach can be discussed and interpreted. In the case of harmonic temperature-, stress- or strain-controlled excitations, the corresponding relations of the responses of the material were computed in closed form. In comparison with other approaches proposed in literature (see, e.g., Refs. [2,29,32] for a "correspondence principle-based" frequency-domain approach) the model proposed in the current paper is a time-domain formulation. The advantage of this approach is that explicit relations for the complex frequency-dependent response functions in combination with their dependence on the material parameters are obtained.

7.1. Stress- and temperature-controlled processes

If a sinusoidal temperature excitation is prescribed and the stress perturbation is set to zero the response of the material is given by the complex specific heat (7.1) in combination with the complex coefficient of thermal expansion (7.2):

$$\hat{c}_p(\omega) = c_{p0} + \theta_{\text{ref}}\,\underline{e} \cdot \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{e} \tag{7.1}$$

Table 2
Asymptotic properties of the model under harmonic stress and temperature control.

High frequencies	Low frequencies
$\hat{c}_p(\infty) = c_{p0}$	$\hat{c}_p(0) = c_{p0} + \theta_{\text{ref}}\underline{e} \cdot \underline{\underline{d}}^{-1}\underline{e}$
$\hat{\kappa}(\infty) = \kappa_0$	$\hat{\kappa}(0) = \kappa_0 + \rho\underline{w} \cdot \underline{\underline{d}}^{-1}\underline{e}$
$\hat{J}(\infty) = 1/E_0$	$\hat{J}(0) = \frac{1}{E_0} + \rho\underline{w} \cdot \underline{\underline{d}}^{-1}\underline{w}$

$$\hat{\kappa}(\omega) = \kappa_0 + \rho\underline{w} \cdot \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{e} \tag{7.2}$$

If, on the other hand, a harmonic stress excitation is prescribed and the temperature change is zero, the response of the material is determined by the frequency-dependent compliance:

$$\hat{J}(\omega) = \frac{1}{E_0} + \rho\underline{w} \cdot \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\,\underline{w} \tag{7.3}$$

Comparing these relations, comparable structures and frequency dependences are recognised. Using the transfer-matrix method in combination with the theory of analytic functions, the following statement was derived in Ref. [32]: if $\hat{c}_p(\omega) - c_{p0}$ and $\hat{\kappa}(\omega) - \kappa_0$ are known for all frequencies, then $\hat{J}(\omega) - 1/E_0$ can be calculated. In the context of the model developed in the current paper, this result can be substantiated with the dependence of specific heat, thermal expansion coefficient and compliance on the same original set of material parameters which are contained in the Gibbs free energy and the evolution laws for the internal variables.

The specific heat at constant stress $\hat{c}_p(\omega)$ is frequency-dependent only if the temperature-driven term in the evolution laws of the internal variables is not zero. This term depends on the material parameter vector $\underline{e}$ which describes the coupling between the temperature and the internal variables in the Gibbs free energy (3.22). The compliance $\hat{J}(\omega)$ depends on the frequency only if the parameter vector $\underline{w}$ differs from zero. It describes the coupling between the stress and the internal variables. But the coefficient of thermal expansion $\hat{\kappa}(\omega)$ depends on the frequency only if both couplings between internal variables and stress and between internal variables and temperature do not vanish, i.e. if the necessary conditions $\underline{e} \neq \underline{0}$ and $\underline{w} \neq \underline{0}$ are satisfied. If, on the other hand, a given material exhibits a frequency-dependent coefficient of thermal expansion like polystyrene [9,10] then $\underline{e} \neq \underline{0}$ as well as $\underline{w} \neq \underline{0}$ must hold for a proper description. As a consequence, both the compliance and the specific heat are frequency-dependent in the model. In standard models of linear thermoviscoelasticity [4,22] the couplings between the internal variables and the temperature are normally ignored, which corresponds to $\underline{e} = \underline{0}$ in the developed model. Therefore, the specific heat and the coefficient of thermal expansion exhibit no frequency dependence in those models.

In order to study the asymptotic properties of the response functions (7.1)–(7.3) the following relations which were derived in Ref. [20] are applied:

$$\lim_{\omega\to 0} = \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}} = \underline{\underline{d}}^{-1} \tag{7.4}$$

$$\lim_{\omega\to\infty} = \left(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}} = \underline{\underline{0}} \tag{7.5}$$

A short calculation leads to the low- and high-frequent limits of the specific heat at constant stress, the coefficient of thermal expansion and the compliance.

Taking a look at Table 2 and bearing in mind that the matrix $\underline{\underline{d}}^{-1}$ is positive definite, the well-known behaviour that the specific heat at constant stress reduces when the frequency of the temperature input increases is observed. With increasing frequencies of the stress excitation, the compliance $\hat{J}(\omega)$ also decreases because $\underline{w} \cdot \left(\underline{\underline{d}}^{-1}\underline{w}\right) > 0$ holds for arbitrary parameter vectors $\underline{w}$. The asymptotic behaviour of the coefficient of thermal expansion is different in the sense, that its high-frequent limit can be equal to, smaller or larger than its low-frequent limit. This result stems from the fact that the bilinear-form $\underline{w}\cdot\left(\underline{\underline{d}}^{-1}\underline{e}\right)$ can be either zero, positive or negative.

In order to discuss some consequences of the response functions (7.1)–(7.3) with regard to the Prigogine–Defay ratio (see Ref. [40] for a detailed derivation of this expression), the generalized Cauchy–Schwarz inequality[1] is applied to the bilinear-form $\underline{w}\cdot\left(\underline{\underline{d}}^{-1}\underline{e}\right)$:

$$\left(\underline{w}\cdot\left(\underline{\underline{d}}^{-1}\underline{e}\right)\right)^2 \le \left(\underline{w}\cdot\left(\underline{\underline{d}}^{-1}\underline{w}\right)\right)\left(\underline{e}\cdot\left(\underline{\underline{d}}^{-1}\underline{e}\right)\right) \tag{7.6}$$

Relating the expressions for the asymptotic limits of the response functions for low and high frequencies in Table 2 to the factors in (7.6), the well-known formulation of the so-called linear Prigogine–Defay ratio (see Refs. [34,36,41]) is obtained:

$$1 \le \frac{\rho\left(\hat{c}_p(0)-\hat{c}_p(\infty)\right)\left(\hat{J}(0)-\hat{J}(\infty)\right)}{\theta_{\text{ref}}\left(\hat{\kappa}(0)-\hat{\kappa}(\infty)\right)^2} \tag{7.7}$$

In comparison with formulations given in literature, the mass density ρ occurs in (7.7) since in this paper mass-specific quantities are used. This inequality makes a statement about the magnitude of the changes in the response functions of glass-forming materials for infinitely small and high frequencies. It contains only the asymptotic limits of the response functions, but it is independent on the frequency. For a detailed discussion in this context, the reader is referred to Refs. [30,32,34,38]. In Ref. [34], a frequency-dependent linear dynamic Prigogine–Defay ratio is defined on the basis of the imaginary parts of the response functions. To this end, the decomposition of the matrix

$$\begin{aligned}\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}} &= \left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}} - i\omega\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\\ &= \mathrm{Re}\left(\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\right) - i\,\mathrm{Im}\left(\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\right)\end{aligned} \tag{7.8}$$

into real and imaginary parts is needed (see Ref. [20]). In Appendix D, it is shown that both parts of (7.8) are positive definite for $\omega > 0$. Using this result, the imaginary parts of (7.1)–(7.3) can be computed:

$$\mathrm{Im}\left(\hat{c}_p\right) = \omega\theta_{\text{ref}}\,\underline{e}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{e} \tag{7.9}$$

$$\mathrm{Im}\left(\hat{\kappa}\right) = \rho\omega\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{e} \tag{7.10}$$

$$\mathrm{Im}\left(\hat{J}\right) = \rho\omega\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{w} \tag{7.11}$$

The application of the Cauchy–Schwarz inequality to the bilinear-form in (7.10) leads to

$$\begin{aligned}\left(\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{e}\right)^2 \le{}& \left(\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{w}\right)\\ &\times\left(\underline{e}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{e}\right)\end{aligned} \tag{7.12}$$

and finally to the frequency-dependent linear dynamic Prigogine–Defay ratio:

$$1 \le \frac{\rho\,\mathrm{Im}\left(\hat{c}_p(\omega)\right)\mathrm{Im}\left(\hat{J}(\omega)\right)}{\theta_{\text{ref}}\left(\mathrm{Im}\left(\hat{\kappa}(\omega)\right)\right)^2} \tag{7.13}$$

The advantages of this frequency-dependent expression are discussed in detail in Ref. [34]. In this reference, it has been shown, that only one single internal variable is needed to describe the dynamic behaviour of the glass-forming material, when the ratio (7.13) is equal to one.

Since the real part of the matrix (7.8) is also positive definite, the generalized Cauchy–Schwarz inequality can be applied again:

$$\begin{aligned}\left(\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}\,\underline{e}\right)^2 \le{}& \left(\underline{w}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}\,\underline{w}\right)\\ &\times\left(\underline{e}\cdot\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}\,\underline{e}\right)\end{aligned} \tag{7.14}$$

This leads to a different version of a frequency-dependent Prigogine–Defay ratio:

$$1 \le \frac{\rho\,\mathrm{Re}\left(\hat{c}_p(\omega)-c_{p0}\right)\mathrm{Re}\left(\hat{J}(\omega)-1/E_0\right)}{\theta_{\text{ref}}\left(Re\left(\hat{\kappa}(\omega)\right)-\kappa_0\right)^2} \tag{7.15}$$

7.2. Strain- and temperature-controlled processes

If a harmonic temperature excitation is prescribed and the strain perturbation is set to zero, the response of the material is determined by the frequency-dependent specific heat at constant strain (7.16) in combination with the thermal modulus (7.17):

$$\begin{aligned}\hat{c}_v(\omega) = c_{p0} - \frac{\theta_{\text{ref}}E_0\kappa_0^2}{\rho} &+ \theta_{\text{ref}}\left(\underline{e}-E_0\kappa_0\underline{w}\right)\\ &\cdot\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\left(\underline{e}-E_0\kappa_0\underline{w}\right)\end{aligned} \tag{7.16}$$

$$\hat{\mu}(\omega) = -E_0\left(\kappa_0+\rho\underline{w}\cdot\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\left(\underline{e}-E_0\kappa_0\underline{w}\right)\right). \tag{7.17}$$

If, on the other hand, a harmonic strain excitation is prescribed and the temperature change is set to zero, the response of the material is determined by the complex modulus:

$$\hat{E}(\omega) = E_0\left(1-\rho E_0\underline{w}\cdot\left(\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\,\underline{w}\right)\right) \tag{7.18}$$

Taking a look at the specific heat at constant strain (7.16) a remarkable effect is observed: if there is no direct coupling between the temperature and the changes in the internal variables, i.e. $\underline{e}=\underline{0}$ is assumed, the specific heat at constant stress $\hat{c}_p(\omega)$ as specified in (7.1) becomes frequency-independent, but $\hat{c}_v(\omega)$ remains frequency-dependent. In this case, (7.16) leads to

$$\hat{c}_v(\omega) = c_{p0} - \frac{\theta_{\text{ref}}E_0\kappa_0^2}{\rho} + \theta_{\text{ref}}E_0^2\kappa_0^2\underline{w}\cdot\left(i\omega\underline{\underline{1}}+\underline{\underline{A}}\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\right)^{-1}\underline{\underline{A}}\,\underline{w}. \tag{7.19}$$

The physical interpretation in the case of $\underline{e}=\underline{0}$ in combination with $\underline{w}\neq\underline{0}$ is as follows. The harmonic temperature change induces

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[1] The generalized Cauchy–Schwarz inequality applies for positive semidefinite matrices $\underline{\underline{H}}$ and vectors $\underline{x},\underline{y}\neq\underline{0}$: $\left(\underline{x}\cdot\left(\underline{\underline{H}}\,\underline{y}\right)\right)^2 \le \left(\underline{x}\cdot\left(\underline{\underline{H}}\,\underline{x}\right)\right)\left(\underline{y}\cdot\left(\underline{\underline{H}}\,\underline{y}\right)\right)$.

oscillating stresses if the strain is zero, i.e. if $\chi = 0$ is prescribed. Since $\underline{w} \neq \underline{0}$ is assumed, the coupling between the stress and the internal variables takes place such that the specific heat $\hat{c}_v(\omega)$ becomes frequency-dependent. Under the same assumption, the coefficient of thermal expansion (7.2) becomes frequency-independent but the thermal modulus depends on the frequency. In this case, (7.17) leads to

$$\hat{\mu}(\omega) = -E_0 \left(\kappa_0 - \rho E_0 \kappa_0 \underline{w} \cdot \left(i\omega \underline{\underline{1}} + \underline{\underline{A}} \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w} \right) \right)^{-1} \underline{\underline{A}}\,\underline{w} \right). \tag{7.20}$$

Now, for comparison, $\underline{e} \neq \underline{0}$ and $\underline{w} = \underline{0}$ is supposed. In this case, there is no direct coupling between stress and internal variables but a direct coupling between temperature and internal variables. Under this assumption, (7.18) and (7.3) lead to $\hat{E}(\omega) = E_0$ and $\hat{J}(\omega) = 1/E_0$ such that the modulus and the compliance become frequency-independent. From the mechanical point of view, such a material can be characterised as linear elastic. Due to the assumption of $\underline{w} = \underline{0}$ the specific heat at constant strain (7.16) remains frequency-dependent:

$$\hat{c}_v(\omega) = c_{p0} - \frac{\theta_{\mathrm{ref}} E_0 \kappa_0^2}{\rho} + \theta_{\mathrm{ref}}\, \underline{e} \cdot \left(i\omega \underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}} \right)^{-1} \underline{\underline{A}}\,\underline{e} \tag{7.21}$$

Taking a look at (7.1), it is seen that the specific heat at constant stress is not influenced, i.e. both specific heats exhibit the same frequency dependence in this case.

If $\underline{e} = \underline{0}$ and $\underline{w} = \underline{0}$ is chosen, no couplings at all occur. Hence the frequency dependence vanishes and the standard expressions of a linear thermoelastic material are obtained:

$$\hat{c}_p = c_{p0}, \quad \hat{c}_v = c_{p0} - \frac{\theta_{\mathrm{ref}} E_0 \kappa_0^2}{\rho}, \quad \hat{J} = \frac{1}{E_0}, \quad \hat{E} = E_0, \quad \hat{\kappa} = \kappa_0, \quad \hat{\mu} = -E_0 \kappa_0 \tag{7.22}$$

In the asymptotic cases of low- and high-frequent excitations, (7.4) and (7.5) can be applied in the corresponding sense.

The results for the low- and high-frequent limits of the specific heat at constant strain, the thermal and the mechanical modulus are listed in Table 3.

Since $\underline{x} \cdot \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w} \right) \underline{x} = \underline{x} \cdot \underline{\underline{d}}\,\underline{x} + \rho E_0 (\underline{x} \cdot \underline{w})^2 > 0$ holds for arbitrary vectors $\underline{x} \neq \underline{0}$, the inverse matrix $\left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w} \right)^{-1}$ exists as well and is also positive definite. This property shows that the mechanical modulus reduces as the frequency is reduced. The specific heat at constant strain also lessens as function of frequency, but the thermal modulus can increase or decrease depending on the sign of the bilinear-form $\underline{w} \cdot \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w} \right)^{-1} (\underline{e} - E_0 \kappa_0 \underline{w})$.

The application of the generalized Cauchy–Schwarz inequality to the frequency-dependent response functions (7.16)–(7.18) for strain- and temperature-controlled processes is also possible and leads to a different set of Prigogine–Defay ratios similar to (7.7), (7.13) and (7.15). The interested reader is also referred to Ref. [34].

8. Conclusions

In this essay, a new constitutive model has been developed to represent the dynamic material behaviour of viscoelastic media in the neighbourhood of the glass transition. In this region, a frequency-dependence of the specific heat, the coefficient of thermal expansion and the mechanical material behaviour is observed as published in literature [8–10,13,16]. The physical reason for this type of material behaviour is the fact that the molecular mobility is influenced by changes in temperature-, strain- or stress. In the neighbourhood of the glass transition, viscoelastic media are highly sensitive with respect to mechanical or thermal perturbations. In the case of low-frequent stress-, strain- or temperature-controlled excitations, the molecules follow the excitation, whereas for much higher frequencies they are frozen. In between the limiting cases, the molecular motions follow with frequency-dependent amplitudes and phase shifts.

In order to represent these phenomena simultaneously in a single constitutive approach, the theory of thermodynamics with internal variables was applied. The Gibbs free energy per unit mass was taken as thermodynamic potential. It depends on the stress, the temperature and a set of internal variables in order to describe the history dependence of the material. In the neighbourhood of the thermodynamic equilibrium, the Gibbs free energy is represented by a quadratic approximation in the changes in stress, temperature and internal variables. The evolution equations for the internal state variables were formulated taking into account the thermodynamic dissipation principle. As a result of this approach, the temporal evolution of the internal variables is driven by the changes in both the temperature and the stress. For the purpose of calculating the frequency-dependent specific heat at constant stress or strain, the coefficient of thermal expansion, the thermal modulus and the mechanical compliance and modulus, harmonic stress, strain or temperature excitations were prescribed. Based on the computed relations, the following statements and interpretations can be made:

- The frequency-dependent specific heat at constant stress is determined by the material parameters which express the influence of the temperature on the evolution of the internal state variables. These material parameters also describe the coupling between the temperature and the internal variables in the Gibbs free energy.
- The frequency-dependent specific heat at constant strain depends on both the material constants which describe the influence of the temperature on the internal variables and the parameters describing the influence of the stress on the internal variables. Thus, a material whose specific heat at constant stress is independent on the frequency, i.e. a direct coupling between the temperature and the internal variables does not occur, can nevertheless exhibit a frequency-dependent specific heat at constant strain: if the strain is constant, a harmonic temperature excitation induces a harmonic stress which leads to oscillations in the internal state variables and, therefore, to a frequency-dependence of the specific heat at constant strain.
- The coefficient of thermal expansion is frequency-dependent only if there is at least one internal state variable whose evolution is driven simultaneously by temperature and stress. If, for a given material, the coefficient of thermal expansion is frequency-independent, then there are no internal variables or molecular mechanisms which are driven by both the stress and the temperature. Nevertheless, such a material can exhibit frequency-dependent mechanical properties or a frequency-dependent specific heat. However, if the coefficient of thermal expansion of a given material depends on the frequency, this material shows both frequency-dependent mechanical properties and a frequency-dependent specific heat at constant stress.
- The thermal modulus depends on the frequency, if the stress influences the internal variables, i.e. when the material is viscoelastic from the mechanical point of view.
- Both quantities the complex modulus and the compliance depend on the frequency of the corresponding mechanical excitation if the coupling parameters between the strain and the stress, respectively, and the internal state variables do not vanish.
- Frequency-dependent formulations of the Prigogine–Defay ratio as originally proposed in Ref. [34] can be derived from the constitutive approach presented here as well. In addition, a mod-

Table 3
Asymptotic properties of the model under harmonic strain and temperature control.

High frequencies	Low frequencies
$\hat{c}_v(\infty) = c_{p0} - (\theta_{\mathrm{ref}} E_0 \kappa_0^2/\rho)$	$\hat{c}_v(0) = c_{p0} - \frac{\theta_{\mathrm{ref}} E_0 \kappa_0^2}{\rho} + \theta_{\mathrm{ref}} \left(\underline{e} - E_0\kappa_0 \underline{w}\right) \cdot \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w}\right)^{-1} \left(\underline{e} - E_0\kappa_0 \underline{w}\right)$
$\hat{\mu}(\infty) = -E_0\kappa_0$	$\hat{\mu}(0) = -E_0 \left(\kappa_0 + \rho \underline{w} \cdot \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w}\right)^{-1} \left(\underline{e} - E_0\kappa_0 \underline{w}\right)\right)$
$\hat{E}(\infty) = E_0$	$\hat{E}(0) = E_0 \left(1 - \rho E_0 \underline{w} \cdot \left(\underline{\underline{d}} + \rho E_0 \underline{w} \otimes \underline{w}\right)^{-1} \underline{w}\right)$

ification of the Prigogine–Defay ratio connecting the real parts of the response functions has been formulated.

For the experimental validation of the proposed theory and its consequences, it is necessary to consider one and the same material, to measure the frequency-dependence of specific heat at constant stress, the thermal expansion behaviour and the dynamic modulus or compliance in the neighbourhood of the glass transition and to identify the material constants. In a recent article, published in 2008, Pedersen et al. [41], remark in this context: “Unfortunately, the relevant frequency-dependent thermoviscoelastic response functions are difficult to measure - in fact, no reliable measurements appear yet to exist”.

In order to reduce the arithmetic formalism and to work out the main physical ideas, the proposed model considers only one-dimensional states of stress and strain so far. But in the near future, the approach will be generalized to develop a three-dimensional theory, in which tensorial states of stress and strain can be taken into account.

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Appendix A. Equations of heat conduction formulated with the Gibbs and Helmholtz free energies

Computing the time derivatives of (2.7) and (2.8)

$$\dot{\psi} = \frac{\partial \psi}{\partial \mathbf{E}} \cdot \dot{\mathbf{E}} + \frac{\partial \psi}{\partial \theta}\dot{\theta} + \frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}}, \tag{A.1}$$

$$\dot{g} = \frac{\partial g}{\partial \mathbf{T}} \cdot \dot{\mathbf{T}} + \frac{\partial g}{\partial \theta}\dot{\theta} + \frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f}, \tag{A.2}$$

and inserting them into the Clausius–Duhem inequalities (2.5) and (2.6) leads to

$$\left(\mathbf{T} - \rho\frac{\partial \psi}{\partial \mathbf{E}}\right) \cdot \dot{\mathbf{E}} - \rho\left(s + \frac{\partial \psi}{\partial \theta}\right)\dot{\theta} - \rho\frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}} - \frac{\vec{q} \cdot \mathrm{grad}(\theta)}{\theta} \geq 0 \tag{A.3}$$

and

$$-\left(\mathbf{E} + \rho\frac{\partial g}{\partial \mathbf{T}}\right) \cdot \dot{\mathbf{T}} - \rho\left(s + \frac{\partial g}{\partial \theta}\right)\dot{\theta} - \rho\frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f} - \frac{\vec{q} \cdot \mathrm{grad}(\theta)}{\theta} \geq 0. \tag{A.4}$$

These inequalities have to be satisfied for arbitrary values of $\dot{\mathbf{E}}$ or $\dot{\mathbf{T}}$ and $\dot{\theta}$. As a result, the following potential relations for the strain and stress tensors and the entropy are obtained:

$$\mathbf{E}\left(\mathbf{T}, \theta, \underline{\alpha}\right) = -\rho\frac{\partial g}{\partial \mathbf{T}} \tag{A.5}$$

$$\mathbf{T}\left(\mathbf{E}, \theta, \underline{\alpha}\right) = \rho\frac{\partial \psi}{\partial \mathbf{E}} \tag{A.6}$$

$$s\left(\mathbf{T}, \theta, \underline{\alpha}\right) = -\frac{\partial g}{\partial \theta} \tag{A.7}$$

$$s\left(\mathbf{E}, \theta, \underline{\alpha}\right) = -\frac{\partial \psi}{\partial \theta} \tag{A.8}$$

The corresponding residual inequalities have to be satisfied by the constitutive equation for the heat flux vector $\vec{q}$ and the evolution equations for the internal variables:

$$-\rho\frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f} - \frac{\vec{q} \cdot \mathrm{grad}(\theta)}{\theta} \geq 0 \tag{A.9}$$

$$-\rho\frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}} - \frac{\vec{q} \cdot \mathrm{grad}(\theta)}{\theta} \geq 0 \tag{A.10}$$

In this essay, it is assumed that the Gibbs and Helmholtz free energies are independent on the temperature gradient. If, in this case, a homogeneous process with $\mathrm{grad}(\theta) = \vec{0}$ is prescribed, the inequalities (A.9) and (A.10) lead to

$$-\rho\frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f} \geq 0, \tag{A.11}$$

$$-\rho\frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}} \geq 0. \tag{A.12}$$

This result shows that the entropy production of the internal variables alone has to be non-negative [22]. Taking (A.1) and (A.2) and the potential relations (A.5)–(A.8) into account, the time rates of the Gibbs and Helmholtz free energies can be reformulated:

$$\rho\dot{g} = -\mathbf{E} \cdot \dot{\mathbf{T}} - \rho s\dot{\theta} + \rho\frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f} \tag{A.13}$$

$$\rho\dot{\psi} = \mathbf{T} \cdot \dot{\mathbf{E}} - \rho s\dot{\theta} + \rho\frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}} \tag{A.14}$$

Inserting these expressions in combination with (A.7) and (A.8) into the corresponding form of the first law of thermodynamics (2.3) or (2.4), the formulations

$$\rho\frac{\partial \psi}{\partial \underline{\alpha}} \cdot \underline{\tilde{f}} = \rho\,\theta\frac{d}{dt}\left(\frac{\partial \psi}{\partial \theta}\right) - \mathrm{div}\left(\vec{q}\right) + \rho r, \tag{A.15}$$

$$\rho\frac{\partial g}{\partial \underline{\alpha}} \cdot \underline{f} = \rho\,\theta\frac{d}{dt}\left(\frac{\partial g}{\partial \theta}\right) - \mathrm{div}\left(\vec{q}\right) + \rho r, \tag{A.16}$$

are obtained. Calculating the time derivatives

$$\frac{d}{dt}\left(\frac{\partial \psi}{\partial \theta}\right) = \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{E}} \cdot \dot{\mathbf{E}} + \frac{\partial^2 \psi}{\partial \theta^2}\dot{\theta} + \frac{\partial^2 \psi}{\partial \theta \partial \underline{\alpha}} \cdot \underline{\tilde{f}}, \tag{A.17}$$

$$\frac{d}{dt}\left(\frac{\partial g}{\partial \theta}\right) = \frac{\partial^2 g}{\partial \theta \partial \mathbf{T}} \cdot \dot{\mathbf{T}} + \frac{\partial^2 g}{\partial \theta^2}\dot{\theta} + \frac{\partial^2 g}{\partial \theta \partial \underline{\alpha}} \cdot \underline{f}, \tag{A.18}$$

inserting them into (A.15) and (A.16) and rearranging the terms finally leads to

$$-\rho\theta\frac{\partial^2 \psi}{\partial \theta^2}\dot{\theta} + \rho\left(\frac{\partial \psi}{\partial \underline{\alpha}} - \theta\frac{\partial^2 \psi}{\partial \theta \partial \underline{\alpha}}\right) \cdot \underline{\tilde{f}} = \rho\theta\frac{\partial^2 \psi}{\partial \theta \partial \mathbf{E}} \cdot \dot{\mathbf{E}} - \mathrm{div}\left(\vec{q}\right) + \rho r, \tag{A.19}$$

$$-\rho\theta\frac{\partial^2 g}{\partial\theta^2}\dot{\theta}+\rho\left(\frac{\partial g}{\partial\underline{\alpha}}-\theta\frac{\partial^2 g}{\partial\theta\partial\underline{\alpha}}\right)\cdot\dot{\underline{f}}=\rho\theta\frac{\partial^2 g}{\partial\theta\partial\mathbf{T}}\cdot\dot{\mathbf{T}}-\mathrm{div}\left(\vec{q}\right)+\rho r. \tag{A.20}$$

These relations are two equivalent formulations of the equation of heat conduction such that the factors of the temperature rate can be interpreted as specific heat at constant stress

$$-\theta\frac{\partial^2 g}{\partial\theta^2}=c_p\left(\mathbf{T},\theta,\underline{\alpha}\right) \tag{A.21}$$

and as specific heat at constant deformation (cf. [22])

$$-\theta\frac{\partial^2\psi}{\partial\theta^2}=c_v\left(\mathbf{E},\theta,\underline{\alpha}\right). \tag{A.22}$$

Appendix B. Formulation of the constitutive model with the Helmholtz free energy

The Helmholtz free energy, can be obtained from the Legendre transformation (2.2) as

$$\psi=g+\frac{1}{\rho}\sigma\varepsilon=g+\frac{1}{\rho}(\sigma_{\mathrm{ref}}+\tau)(\varepsilon_{\mathrm{ref}}+\chi) \tag{B.1}$$

The stress perturbation τ is expressed using (3.23). With (3.22) a short calculation leads to the following expression for the Helmholtz free energy[2]:

$$\begin{aligned}\psi={}&g_{\mathrm{ref}}+\frac{\sigma_{\mathrm{ref}}\ \varepsilon_{\mathrm{ref}}}{\rho}-s_{\mathrm{ref}}\vartheta-\frac{1}{2\theta_{\mathrm{ref}}}\left(c_{p0}-\frac{\theta_{\mathrm{ref}}E_0\kappa_0^2}{\rho}\right)\vartheta^2\\&+\frac{1}{2}\left(\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\underline{\delta}\right)\cdot\underline{\delta}+\frac{\sigma_{\mathrm{ref}}}{\rho}\chi+\left(\underline{e}-E_0\kappa_0\underline{w}\right)\cdot\underline{\delta}\vartheta\\&+\frac{E_0}{2\rho}\chi^2-\frac{E_0\kappa_0}{\rho}\chi\vartheta+E_0\underline{w}\cdot\underline{\delta}\chi\end{aligned} \tag{B.2}$$

Its equilibrium value is $\psi_{\mathrm{ref}}=g_{\mathrm{ref}}+\sigma_{\mathrm{ref}}\varepsilon_{\mathrm{ref}}/\rho$. Using the potential relations for the stress and the entropy listed on the left-hand side of Table 1 in combination with (3.5) and (3.7) the following equations are obtained:

$$\text{Stress}:\tau\left(\chi,\vartheta,\underline{\delta}\right)=E_0\left(\chi-\kappa_0\vartheta+\rho\underline{w}\cdot\underline{\delta}\right) \tag{B.3}$$

$$\begin{aligned}\text{Entropy}:\eta\left(\chi,\vartheta,\underline{\delta}\right)={}&\frac{1}{\theta_{\mathrm{ref}}}\left(c_{p0}-\frac{\theta_{\mathrm{ref}}E_0\kappa_0^2}{\rho}\right)\vartheta-\left(\underline{e}-E_0\kappa_0\underline{w}\right)\cdot\underline{\delta}\\&+\frac{E_0\kappa_0}{\rho}\chi\end{aligned} \tag{B.4}$$

Comparing the expression (3.23) for the strain with (B.3) determining the stress, it can be recognised that both are equal. Considering this and comparing the relations for the entropy (B.4) and (3.24) they are also equal. The specific heat at constant strain is calculated using

$$c_v\left(\chi,\vartheta,\underline{\delta}\right)=-\left(\theta_{\mathrm{ref}}+\vartheta\right)\frac{\partial^2\psi}{\partial\vartheta^2}=\left(1+\frac{\vartheta}{\theta_{\mathrm{ref}}}\right)\left(c_{p0}-\frac{\theta_{\mathrm{ref}}E_0\kappa_0^2}{\rho}\right). \tag{B.5}$$

The corresponding evolution law for the changes in the internal state variables is obtained by inserting (B.3) into (3.25):

$$\dot{\underline{\delta}}=-\underline{\underline{A}}\left(\left(\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w}\right)\underline{\delta}+\left(\underline{e}-E_0\kappa_0\underline{w}\right)\vartheta+E_0\underline{w}\chi\right) \tag{B.6}$$

Now, some substitutions in the Helmholtz free energy and the evolution laws for the internal variables are introduced such that the form of the representation becomes similar to the form of the representation with the Gibbs free energy:

$$\begin{aligned}\psi={}&\psi_{\mathrm{ref}}-s_{\mathrm{ref}}\vartheta-\frac{c_{v0}}{2\theta_{\mathrm{ref}}}\vartheta^2+\frac{\left(\tilde{\underline{\underline{d}}}\underline{\delta}\right)\cdot\underline{\delta}}{2}+\frac{\sigma_{\mathrm{ref}}}{\rho}\chi+\tilde{\underline{e}}\cdot\underline{\delta}\vartheta+\frac{E_0\chi^2}{2\rho}\\&-\frac{E_0\kappa_0}{\rho}\chi\vartheta+E_0\underline{w}\cdot\underline{\delta}\chi\end{aligned} \tag{B.7}$$

$$\dot{\underline{\delta}}=-\underline{\underline{A}}\left(\tilde{\underline{\underline{d}}}\underline{\delta}+\tilde{\underline{e}}\vartheta+E_0\underline{w}\chi\right) \tag{B.8}$$

$$c_{v0}=c_{p0}-\frac{\theta_{\mathrm{ref}}E_0\kappa_0^2}{\rho} \tag{B.9}$$

$$\tilde{\underline{\underline{d}}}=\underline{\underline{d}}+\rho E_0\underline{w}\otimes\underline{w} \tag{B.10}$$

$$\tilde{\underline{e}}=\underline{e}-E_0\kappa_0\underline{w} \tag{B.11}$$

In this formulation, the changes in stress and entropy and the rates of the internal variables are linear functions of the changes in strain, temperature and internal variables.

Appendix C. Evaluation of the heat conduction equations for prescribed temperature processes

Following Ref. [20], space-independent conditions are postulated and it is assumed that the temperature history of a homogeneous specimen of the mass $\Delta m=\rho\Delta V$ is prescribed. The absorbed or emitted heat power P_{DSC} which is required to realise the temperature history can be calculated by evaluating the balance equation of energy (see [24]). Considering the Gaussian theorem of integration, the terms on the right-hand side of (4.1) and (4.2) are equal to the heat power per unit mass $P_{\mathrm{DSC}}/\Delta m$ which is supplied to the specimen over its surface.

$$\begin{aligned}-\frac{1}{\rho}\mathrm{div}\left(\vec{q}\right)&=-\frac{\Delta V\mathrm{div}\left(\vec{q}\right)}{\Delta m}=\frac{-1}{\Delta m}\int_{\Delta V}\mathrm{div}\left(\vec{q}\right)dV=\frac{-1}{\Delta m}\int_{\Delta V}\vec{q}\cdot\vec{n}dA\\&=\frac{P_{\mathrm{DSC}}}{\Delta m}\end{aligned} \tag{C.1}$$

Now, the free energies are differentiated with respect to temperature and internal variables. To this end, $\tau=0$ is assumed in the case of (3.22) and $\chi=0$ in the case of (B.7). Using (3.22), (3.25), (B.7) and (B.8) the following results are obtained:

$$\begin{aligned}&\left(\frac{\partial g}{\partial\underline{\delta}}-\left(\theta_{\mathrm{ref}}+\vartheta\right)\frac{\partial^2 g}{\partial\vartheta\partial\underline{\delta}}\right)\cdot\dot{\underline{\delta}}=-\underline{\delta}\cdot\left[\left(\underline{\underline{dAd}}\right)\underline{\delta}\right]-\underline{\delta}\cdot\left[\left(\underline{\underline{dA}}\right)\underline{e}\right]\vartheta\\&+\theta_{\mathrm{ref}}\ \underline{e}\cdot\left(\underline{\underline{A}}\underline{e}\right)\vartheta+\theta_{\mathrm{ref}}\ \underline{e}\cdot\left[\left(\underline{\underline{Ad}}\right)\underline{\delta}\right]\end{aligned} \tag{C.2}$$

$$\begin{aligned}&\left(\frac{\partial\psi}{\partial\underline{\delta}}-\left(\theta_{\mathrm{ref}}+\vartheta\right)\frac{\partial^2\psi}{\partial\vartheta\partial\underline{\delta}}\right)\cdot\dot{\underline{\delta}}=-\underline{\delta}\cdot\left[\left(\underline{\underline{\tilde{d}A\tilde{d}}}\right)\underline{\delta}\right]-\underline{\delta}\cdot\left[\left(\underline{\underline{\tilde{d}A}}\right)\tilde{\underline{e}}\right]\vartheta\\&+\theta_{\mathrm{ref}}\ \tilde{\underline{e}}\cdot\left(\underline{\underline{A}}\tilde{\underline{e}}\right)\vartheta+\theta_{\mathrm{ref}}\ \tilde{\underline{e}}\cdot\left[\left(\underline{\underline{A\tilde{d}}}\right)\underline{\delta}\right]\end{aligned} \tag{C.3}$$

Calculating the second derivatives of ψ and g with respect to the temperature change,

$$-\left(\theta_{\mathrm{ref}}+\vartheta\right)\frac{\partial^2 g}{\partial\vartheta^2}=\left(1+\frac{\vartheta}{\theta_{\mathrm{ref}}}\right)c_{p0}, \tag{C.4}$$

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[2] The dyadic product in the form of $\left(\underline{w}\cdot\underline{\delta}\right)^2=\left(\left(\underline{w}\cdot\underline{\delta}\right)\underline{w}\right)\cdot\underline{\delta}=\left(\left(\underline{w}\otimes\underline{w}\right)\underline{\delta}\right)\cdot\underline{\delta}$ has been used.

$$-\left(\theta_{\text{ref}}+\vartheta\right)\frac{\partial^2\psi}{\partial\vartheta^2}=\left(1+\frac{\vartheta}{\theta_{\text{ref}}}\right)c_{v0}, \tag{C.5}$$

and inserting all these expressions into (4.1) and (4.2), the following relations are obtained:

$$\text{Constant stress}: c_{p0}\dot{\vartheta}+\theta_{\text{ref}}\,\underline{e}\cdot\left(\underline{\underline{A}}\left(\underline{e}\vartheta+\underline{\underline{d}\delta}\right)\right)+c_{p0}\frac{\vartheta}{\theta_{\text{ref}}}\dot{\vartheta}$$

$$-\underline{\delta}\cdot\left(\underline{\underline{dA}}\left(\underline{\underline{d}\delta}+\underline{e}\vartheta\right)\right)=\frac{P_{\text{DSC}}(t)}{\Delta m} \tag{C.6}$$

$$\text{Constant strain}: c_{v0}\dot{\vartheta}+\theta_{\text{ref}}\,\underline{\tilde{e}}\cdot\left(\underline{\underline{A}}\left(\underline{\tilde{e}}\vartheta+\underline{\underline{\tilde{d}}\delta}\right)\right)+c_{v0}\frac{\vartheta}{\theta_{\text{ref}}}\dot{\vartheta}$$

$$-\underline{\delta}\cdot\left(\underline{\underline{\tilde{d}A}}\left(\underline{\underline{\tilde{d}}\delta}+\underline{\tilde{e}}\vartheta\right)\right)=\frac{P_{\text{DSC}}(t)}{\Delta m} \tag{C.7}$$

Appendix D. Positive definiteness of matrices

In order to prove that the matrix

$$\underline{\underline{B}}=\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}} \tag{D.1}$$

is positive definite its inverse

$$\underline{\underline{B}}^{-1}=\underline{\underline{A}}^{-1}\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)=\omega^2\underline{\underline{A}}^{-1}+\underline{\underline{d}}\,\underline{\underline{A}}\,\underline{\underline{d}} \tag{D.2}$$

is considered and its positive definiteness is demonstrated. Since the matrices $\underline{\underline{A}}$ and $\underline{\underline{d}}$ are positive definite and symmetric, their inverses exist as well and are also symmetric and positive definite. Thus, the following relation holds for arbitrary column vectors $\underline{x}\neq\underline{0}$:

$$\underline{x}\cdot\left(\underline{\underline{B}}^{-1}\underline{x}\right)=\omega^2\underline{x}\cdot\underline{\underline{A}}^{-1}\underline{x}+\underline{x}\cdot\left(\underline{\underline{d}}\,\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{x}\right)=\omega^2\underbrace{\underline{x}\cdot\underline{\underline{A}}^{-1}\underline{x}}_{>0}$$

$$+\underbrace{\left(\underline{\underline{d}}\,\underline{x}\right)\cdot\underline{\underline{A}}\left(\underline{\underline{d}}\,\underline{x}\right)}_{>0}>0 \tag{D.3}$$

Since $\underline{\underline{B}}^{-1}$ is positive definite the matrix $\underline{\underline{B}}$ defined in (D.1) is also positive definite. Thus, the imaginary part of (7.8) is positive definite for $\omega>0$ and positive semi-definite for $\omega\geq 0$.

In order to show the positive definiteness of the matrix

$$\underline{\underline{C}}=\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}, \tag{D.4}$$

its inverse is considered:

$$\underline{\underline{C}}^{-1}=\left(\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}\right)^{-1}\left(\omega^2\underline{\underline{1}}+\left(\underline{\underline{A}}\,\underline{\underline{d}}\right)^2\right)=\omega^2\underline{\underline{A}}^{-1}\underline{\underline{d}}^{-1}\underline{\underline{A}}^{-1}+\underline{\underline{d}} \tag{D.5}$$

Assuming an arbitrary vector $\underline{x}\neq\underline{0}$, the relation

$$\underline{x}\cdot\underline{\underline{C}}^{-1}\underline{x}=\omega^2\underline{x}\cdot\underline{\underline{A}}^{-1}\underline{\underline{d}}^{-1}\underline{\underline{A}}^{-1}\underline{x}+\underline{x}\cdot\underline{\underline{d}}\,\underline{x}=\omega^2\underbrace{\left(\underline{\underline{A}}^{-1}\underline{x}\right)\cdot\underline{\underline{d}}^{-1}\left(\underline{\underline{A}}^{-1}\underline{x}\right)}_{>0}$$

$$+\underbrace{\underline{x}\cdot\underline{\underline{d}}\,\underline{x}}_{>0}>0 \tag{D.6}$$

holds and demonstrates the positive definiteness of $\underline{\underline{C}}^{-1}$ and also that of the matrix $\underline{\underline{C}}$ defined in (D.4).

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