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On the frequency-dependent specific heat and TMDSC: Constitutive modelling based on thermodynamics with internal state variables

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ABSTRACT

To develop constitutive models to represent the thermomechanically chemically coupled behaviour of curing resins, vulcanizing elastomers or melting and crystallizing polymers the technique of DSC is extremely helpful. In the present study, the method of TMDSC is interpreted and evaluated in the context of thermodynamics with internal state variables. The balance equation of energy and the dissipation principle in the form of the Clausius–Duhem inequality form the theoretical basis of our study. Since the pressure and the temperature are the external variables in DSC, the specific Gibbs free energy is used as thermodynamic potential. It depends on temperature, stress and a set of internal state variables to represent the microstructure of the material on a phenomenological basis. The temperature- and internal variable-induced changes in the Gibbs free energy are approximated by a Taylor series up to second order terms. As a substantial result of this work, closed-form expressions for the dynamic calorimetric response due to harmonic temperature perturbations and the frequency-dependent complex heat capacity are derived. The theory allows a physical interpretation of the complex heat capacity and its underlying phenomena and is in accordance with experimental observations from literature.

1. Introduction

Differential scanning calorimetry, usually abbreviated with the acronym DSC, is a well-established experimental technique. It is frequently applied to analyse temperature-dependent changes in the specific enthalpy of materials or to study the kinetics of chemical reactions (see e.g., refs. [23,24]). Changes in the enthalpy come to light, on the one hand, by the heat capacity of the material and, on the other hand, by strain- or temperature-driven exo- or endothermal changes in the microstructure like crystallization, phase transitions or chemical reactions (e.g., ref. [15]). These changes can be reversible or irreversible, rate-dependent or rate-independent. In the industry, the DSC technique is often applied to compare the quality of materials. For more information about DSC and its technical realisation we refer the reader to the comprehensive textbook of Höhne et al. [10].

In conventional DSC investigations, constant or linear time-dependent temperature histories are prescribed and in temperature-modulated differential scanning calorimetry, abbreviated as TMDSC, sinusoidal temperature changes with small amplitudes are superimposed (see e.g., refs. [2,4,6,11,14,18,22,25,26,29]). In the, recently developed, technique of general temperature-modulated differential scanning calorimetry (GTMDSC) an arbitrary periodic temperature signal with small amplitude is added to the constant or linearly changing base temperature (cf. [6,17]).

To interpret the experimental data of conventional DSC analyses there is a huge amount of technical literature, but to interpret frequency-dependent TMDSC measurements there are still open questions and thus many recent publications. For example in ref. [27] the influence of temperature-induced strains and the relaxation of the resulting stresses on the frequency-dependent heat capacity of highly viscous polymer liquids is studied with regard to the experimental technique used in ref. [1]. Physically, the frequency dependence of the specific heat can be attributed to temperature-induced changes in the microstructure of the material (see e.g., refs. [29,30]). Several authors argue with the linear or non-linear response theory (see e.g., refs. [17,20,21]) which is rather similar to the theory of linear viscoelasticity in the time- or the frequency-domain. This approach leads in a quite natural way to the concept of a complex heat capacity with real and imaginary parts. An alternative concept which is based on an order parameter is given in ref. [13]. A physically based approach in order to interpret TMDSC data which is based on non-equilibrium thermodynamics is developed in the excellent and comprehensive review article [7] (see also ref. [8]). An interesting interpretation of the imaginary part of the heat capacity in terms of temperature-heat ellipses is provided in ref. [12]. Many authors state, that the physical meaning of the complex heat capacity is still unclear and a subject of discussion. Other authors study or model the experimental procedure of

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TMDSC (e.g., ref. [18]) and the measuring equipment in very detail and solve the differential equation of heat conduction to calculate the complex heat capacity of the material under consideration (cf. [3]). The reason for the studies of this type is the elimination of the heat conduction-induced phase shift between the specimen temperature and the signal of the calorimeter. These technical effects are not discussed in the current paper.

Nomenclature

a, b, c_{p0}	scalar material parameters of the approximation of the Gibbs free energy
$\underset{\approx}{A}$	material parameter matrix of the evolution equations for the internal variables
$\underset{\sim}{c}, \underset{\sim}{e}$	material parameter vectors of the approximation of the Gibbs free energy
$\underset{\approx}{d}$	material parameter matrix of the approximation of the Gibbs free energy
$\mathrm{div}(\cdot)$	divergence operator: $\mathrm{div}(\vec{q}) = \partial q_1/\partial x_1 + \partial q_2/\partial x_2 + \partial q_3/\partial x_3$
e, h, s	specific internal energy, enthalpy and entropy per unit mass
$\exp(\underset{\approx}{X})$	matrix exponential function: $\exp(\underset{\approx}{X}) = \sum_{k=0}^{\infty} \underset{\approx}{X}^k/k!$
$f_k(\cdots)$	right-hand side of the differential equation for the internal state variable α_k
$\underset{\sim}{f}$	column vector of the functions f_k: $\underset{\sim}{f} = (f_1, \ldots, f_n)^{\mathrm{T}}$
g_0, s_0	Gibbs free energy and entropy belonging to the thermodynamic equilibrium
$\mathrm{grad}(\cdot)$	gradient operator: $\mathrm{grad}(\theta) = (\partial\theta/\partial x_1)\vec{e}_1 + (\partial\theta/\partial x_2)\vec{e}_2 + (\partial\theta/\partial x_3)\vec{e}_3$
$\Delta m, \Delta V, \rho$	mass, volume and mass density of the sample
$P_{\mathrm{ref}}, P_{\mathrm{mat}}$	power absorbed by the reference tin and the sample tin
P_{DSC}	power absorbed by the sample
$\vec{q}, r$	heat flux vector and volume-distributed heat supply per unit mass
$\mathrm{Re}(z), \mathrm{Im}(z)$	real and imaginary parts of a complex number z
ΔS_{cycl}	entropy production during a temperature cycle
t, ω	time and angular frequency
$\mathbf{T}, \mathbf{E}, \dot{\mathbf{T}}, \dot{\mathbf{E}}$	stress and strain tensor and their time derivatives
$\vec{x} \cdot \vec{y}$	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: $\underset{\sim}{x} \cdot \underset{\sim}{y} = \sum_{k=1}^{n} x_k y_k$
$\underset{\approx}{X}^{-1}$	inverse of the $n \times n$ matrix $\underset{\approx}{X}$: $\underset{\approx}{X}\underset{\approx}{X}^{-1} = \underset{\approx}{1}$
$\mathbf{X} \cdot \mathbf{Y}$	scalar product between two second order tensors: $\mathbf{X} \cdot \mathbf{Y} = \sum_{i,k=1}^{3} X_{ik} Y_{ik}$
$\underset{\approx}{1}$	unit matrix of dimension $n \times n$

Greek symbols

$\vartheta(t), \hat{\vartheta}$	time-dependent temperature perturbation and its amplitude
α_k	scalar internal state variable
$\underset{\sim}{\alpha}$	column vector of the internal state variables: $\underset{\sim}{\alpha} = (\alpha_1, \ldots, \alpha_n)^{\mathrm{T}}$
$\underset{\sim}{\alpha}_0$	internal variable column vector belonging to the thermodynamic equilibrium
$\underset{\sim}{\delta}(t)$	internal variable changes due to the temperature perturbation
θ	thermodynamic temperature
θ_0	temperature of the thermodynamic equilibrium
ψ, g	specific Helmholtz free energy and Gibbs free energy per unit mass
$\hat{\underset{\sim}{\Delta}}(\omega)$	frequency-dependent transfer function vector of the internal variables $\underset{\sim}{\delta}$

In the present essay, an interpretation of the method of temperature-modulated differential scanning calorimetry in terms of the theory of thermodynamics with internal state variables is provided and an expression for the complex heat capacity is derived. For details concerning the theory of thermodynamics with internal state variables, we refer the reader to [5] and to the comprehensive textbook of Maugin [28]. Our investigation is mainly motivated by the following facts:

- The development of constitutive equations for materials exhibiting process-dependent and thermomechanically chemically coupled material behaviour requires very detailed and comprehensive thermodynamical considerations.
- The physical meaning of the frequency-dependent heat capacity with in-phase and out-of-phase parts is still unclear and, thus, a subject of scientific research and discussion.

The paper is organized as follows: After a brief introduction to DSC, the basic equations of continuum thermodynamics are formulated and the required thermodynamic potentials are defined. Based on the corresponding form of the Clausius–Duhem inequality, it is shown that the Gibbs free energy is the most adequate potential for our investigations. Then, the dynamic calorimetric equation is derived with the Gibbs free energy as thermodynamic potential. The mass-specific Gibbs free energy depends on the stress, the thermodynamic temperature and, in addition, on a set of internal state variables. These variables are introduced to represent temperature-dependent changes in the microstructure of the material and have fading memory properties. Finally, a quadratic approximation of the Gibbs free energy is formulated which is applicable in the vicinity of the thermodynamic state of equilibrium. Based on this approach, expressions for the dynamic calorimetric response and the complex heat capacity are derived and studied. The essay closes with some simulations and a discussion.

1.1. Measuring principle of DSC

Since the measuring principle of DSC is known for many years it is described only roughly in the present paper. For details, we refer the reader to the comprehensive textbook [10]. In order to carry out a DSC analysis, two identical metal tins are prepared: the first tin contains the sample of the material to be studied and the second tin, the reference tin, is empty or contains a neutral reference material. In order to achieve the greatest possible resolution and accuracy, the reference material should have a heat capacity as close as possible to the sample material. Then, both tins are cooled or heated under constant pressure $p = \mathrm{const}$. If the tins have exactly the same heat capacity and the supplied heat fluxes are the same, the temporal evolution of the temperature is the same in both systems. Otherwise, a temperature difference occurs which is measured.

In the following consideration we assume, for simplification, that the reference tin is empty and the supplied heat fluxes are controlled in order to achieve the same temperature evolution in both systems. In the reference system, the heat power P_{ref} is absorbed only by the tin; in the other system P_{mat} is absorbed or emitted by the tin and the sample material. The difference between P_{mat} and

P_{ref} is the DSC-power absorbed or emitted by the sample material:

$$P_{\mathrm{DSC}} = P_{\mathrm{mat}} - P_{\mathrm{ref}} \tag{1.1}$$

In order to relate the DSC-power P_{DSC} to the rate of change in the specific enthalpy, we start with the local balance equation of energy (for details, see ref. [9]):

$$\rho\dot{e} = \mathbf{T}\cdot\dot{\mathbf{E}} - \mathrm{div}(\vec{q}) + \rho r \tag{1.2}$$

The scalars ρ and e are the mass density and the internal energy per unit mass, $\vec{q}$ is the heat flux vector, $\dot{\mathbf{E}}$ the rate of the infinitesimal strain tensor, $\mathbf{T}$ is the Cauchy stress tensor and r is a volume-distributed heat supply[1]. Relation (1.2) is the generalization of the first law of thermodynamics in the form of $\mathrm{d}e = \mathrm{d}w + \mathrm{d}q$ to three-dimensional space- and time-dependent field problems in continuum mechanics.

Expressing the internal energy density e in terms of the specific enthalpy per unit mass

$$h = e - \frac{1}{\rho}\mathbf{T}\cdot\mathbf{E} \quad \Leftrightarrow \quad \rho\dot{e} = \rho\dot{h} + \dot{\mathbf{T}}\cdot\mathbf{E} + \mathbf{T}\cdot\dot{\mathbf{E}} \tag{1.3}$$

leads to the alternative formulation

$$\rho\dot{h} = -\mathbf{E}\cdot\dot{\mathbf{T}} - \mathrm{div}(\vec{q}) + \rho r. \tag{1.4}$$

Now, we consider the relation $\Delta m = \rho\Delta V$ between the mass of the material sample and its volume, assume a constant pressure or state of stress, i.e. $\dot{\mathbf{T}} = \mathbf{0}$, and no volume-distributed heat supply, i.e. $r = 0$. Integration of Eq. (1.4) over the volume of the sample and assuming homogeneous conditions yield

$$\Delta m\dot{h} = -\int_{\Delta V} \mathrm{div}(\vec{q})\mathrm{d}V. \tag{1.5}$$

Application of the Gaussian theorem of integration

$$-\int_{\Delta V} \mathrm{div}(\vec{q})\mathrm{d}V = -\int_{\Delta A} \vec{q}\cdot\vec{n}\mathrm{d}A = P_{\mathrm{DSC}} \tag{1.6}$$

shows that the right-hand side of Eq. (1.5) is equal to the heat power P_{DSC} which is supplied to the material over its surface. The statement on right-hand side of relation (1.6) is based on the assumption that the surface of the sample is directly connected to the heat bath, i.e. energy losses due to heat exchange with the environment are neglected. Finally, we obtain

$$\dot{h} = \frac{P_{\mathrm{DSC}}}{\Delta m} \tag{1.7}$$

which relates the calorimetric response P_{DSC} to the rate of change in the specific enthalpy of the material.

In continuum mechanics, the current state of a material is described by the current values of a set of external and internal state variables. The internal state variables are quantities which are needed, in addition to the external variables, to characterize the current state of the material. Examples are order parameters describing process-induced changes in the microstructure of materials, for example amorphous–crystalline or liquid–solid phase transitions, or variables describing the temporal evolution of chemical reactions. If the external variables change, the internal variables can also change.

Assuming that the external state variables are the thermodynamic temperature and the stress, the dependence of the internal variables $\alpha_1,\ldots,\alpha_n$ on the histories of temperature and stress is modelled by a system of ordinary differential equations in combination with initial conditions (see e.g., refs. [9] or [28]):

$$\dot{\alpha}_k(t) = f_k(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n), \quad \alpha_k(0) = \alpha_{k0}, \quad k = 1, \ldots, n \tag{1.8}$$

Assuming the specific enthalpy $h = h(\mathbf{T}, \theta, \alpha_1,\ldots,\alpha_n)$ to depend on the same variables yields

$$\dot{h} = \frac{\partial h}{\partial \mathbf{T}}\cdot\dot{\mathbf{T}} + \frac{\partial h}{\partial \theta}\dot{\theta} + \sum_{k=1}^{n}\frac{\partial h}{\partial \alpha_k}\dot{\alpha}_k. \tag{1.9}$$

The partial derivative $c_p = \partial h/\partial\theta$ is the heat capacity per unit mass under constant stress. Taking the constant stress tensor $\mathbf{T} = -p\mathbf{1}$ with $p = \mathrm{const}$ into account, we obtain the fundamental equation describing calorimetric responses:

$$\begin{aligned}&\frac{\partial h}{\partial \theta}(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n)\dot{\theta}\\ &\quad + \sum_{k=1}^{n}\frac{\partial h}{\partial \alpha_k}(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n)f_k(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n) = \frac{P_{\mathrm{DSC}}}{\Delta m}\end{aligned} \tag{1.10}$$

The first term in Eq. (1.10) is proportional to the time derivative of the temperature and describes heat capacity-related enthalpy changes. The second term can be attributed to enthalpy changes which are driven by microstructural rearrangements, chemical reactions or phase transitions. Since the sample temperature $\theta(t)$ is a prescribed function of time, the fundamental equation (1.10) in combination with the differential equations (1.8) define a functional of the entire temperature process (see e.g., ref. [16]):

$$\frac{P_{\mathrm{DSC}}(t)}{\Delta m} = \underset{s\geq 0}{\Im}(\theta(t-s)) \tag{1.11}$$

The properties of the functional $\Im$ are determined by the process-dependence of the internal variables $\alpha_1,\ldots,\alpha_n$ with respect to the temperature history. In case of a sinusoidal temperature excitation with constant average and small amplitude, known as TMDSC, the calorimetric response contains one term which is in phase with the temperature and a second term that is in phase with the temperature rate. Based on this property, the idea of a complex heat capacity can easily be motivated.

In fact, Eq. (1.10) is adequate for the physical interpretation of DSC measurements. But to formulate a constitutive theory for the complex heat capacity which is compatible with the second law of thermodynamics, the specific enthalpy is an ill-suited thermodynamic potential. The reason for this deficiency is that the temperature and the stress are not the canonical variables of the specific enthalpy: their canonical variables are the specific entropy s and the stress $\mathbf{T}$. Thus in the following section, Eq. (1.10) is reformulated with the Gibbs free energy as thermodynamic potential. The canonical variables of this potential are the stress tensor $\mathbf{T}$ and the thermodynamic temperature θ.

2. Fundamentals

In addition to the internal energy e and the enthalpy h as specified in Eq. (1.3) there are two further thermodynamic potentials which are frequently applied in continuum mechanics, thermodynamics or physical chemistry. The Helmholtz free energy ψ is defined by

$$\psi = e - \theta s \quad \Leftrightarrow \quad \dot{e} = \dot{\psi} + \dot{\theta}s + \theta\dot{s} \tag{2.1}$$

and the Gibbs free energy g by the relation

$$g = h - \theta s \quad \Leftrightarrow \quad \dot{h} = \dot{g} + \dot{\theta}s + \theta\dot{s}\,. \tag{2.2}$$

The scalar function s is the specific entropy per unit mass. On the basis of Eqs. (2.1) and (2.2) in combination with Eqs. (1.2) and (1.4) two further formulations of the first law of thermodynamics are obtained:

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

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[1] $\mathbf{X}\cdot\mathbf{Y}$ is the scalar product between two second order tensors and $\mathrm{div}(\vec{q})$ is the divergence of a vector field.

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

In continuum mechanics, the second law of thermodynamics is frequently expressed in the form of the Clausius–Duhem inequality which states that the local entropy production γ has to be non-negative (see e.g., [9]). This relation is usually formulated with the Helmholtz free energy ψ as thermodynamic potential:

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

Based on the definitions (1.3), (2.1) and (2.2) of the three other thermodynamic potentials, the following equivalent formulations of Eq. (2.5) are found:

$$\rho\theta\gamma = -\rho\dot{e} + \mathbf{T}\cdot\dot{\mathbf{E}} + \rho\theta\dot{s} - \frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta} \geq 0 \tag{2.6}$$

$$\rho\theta\gamma = -\rho\dot{h} - \mathbf{E}\cdot\dot{\mathbf{T}} + \rho\theta\dot{s} - \frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta} \geq 0 \tag{2.7}$$

$$\rho\theta\gamma = -\rho\dot{g} - \mathbf{E}\cdot\dot{\mathbf{T}} - \rho s\dot{\theta} - \frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta} \geq 0 \tag{2.8}$$

The Clausius–Duhem inequality, in one of the four aforementioned forms (2.5)–(2.8), has to be satisfied by any constitutive model for arbitrary thermomechanical processes. In the case of a given thermodynamic potential e, h, ψ or g the time derivatives of stress or strain and temperature or entropy occur in the particular form of the Clausius–Duhem inequality. This special structure motivates the following set of canonical independent variables of the four thermodynamic potentials:

$$e = e(\mathbf{E}, s, \alpha_1, \ldots, \alpha_n) \tag{2.9}$$

$$h = h(\mathbf{T}, s, \alpha_1, \ldots, \alpha_n) \tag{2.10}$$

$$\psi = \psi(\mathbf{E}, \theta, \alpha_1, \ldots, \alpha_n) \tag{2.11}$$

$$g = g(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n) \tag{2.12}$$

The internal variables $\alpha_1,\ldots\alpha_n$ are additionally introduced to represent the current state of the material if the corresponding external variables are not sufficient. They are determined by a system of ordinary differential equations depending on the selected set of external variables $(\mathbf{E}, s)$, $(\mathbf{T}, s)$, $(\mathbf{E}, \theta)$ or $(\mathbf{T}, \theta)$ and the current values of the internal variables themselves:

$$\dot{\alpha}_k(t) = f_k(\ldots, \alpha_1, \ldots, \alpha_n) \tag{2.13}$$

Other choices of independent variables of the thermodynamic potentials are also possible, for example $h = h(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n)$ instead of $h = h(\mathbf{T}, s, \alpha_1, \ldots, \alpha_n)$, but only in the case of Eqs. (2.9)–(2.12) two potential relations and a simple condition for the compatibility of the model with the second law of thermodynamics are resulting. This is demonstrated for the Gibbs free energy in the following discussion.

Since the stress $\mathbf{T}$ and the temperature θ are the external variables in calorimetric analyses the Gibbs free energy $g = g(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n)$ is the most appropriate thermodynamic potential for our study. Calculating the time derivative of Eq. (2.12)

$$\dot{g} = \frac{\partial g}{\partial \mathbf{T}}\cdot\dot{\mathbf{T}} + \frac{\partial g}{\partial\theta}\dot{\theta} + \sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k \tag{2.14}$$

and inserting this into Eq. (2.8) leads to

$$-\left(\mathbf{E} + \rho\frac{\partial g}{\partial\mathbf{T}}\right)\cdot\dot{\mathbf{T}} - \rho\left(s + \frac{\partial g}{\partial\theta}\right)\dot{\theta} - \rho\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k - \frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta} \geq 0. \tag{2.15}$$

This inequality has to be satisfied for arbitrary numerical values of the rates $\dot{\mathbf{T}}$ and $\dot{\theta}$ of the external variables. As a consequence, the following potential relations for the strain tensor $\mathbf{E}$ and the entropy density s are obtained:

$$\mathbf{E} = -\rho\frac{\partial g}{\partial\mathbf{T}} \tag{2.16}$$

$$s = -\frac{\partial g}{\partial\theta} \tag{2.17}$$

The residual inequality expresses the non-negativity of the local entropy production and has to be satisfied by the constitutive equation for the heat flux vector $\vec{q}$ and the evolution equations (2.13) for the internal variables:

$$\rho\theta\gamma = -\rho\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k - \frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta} \geq 0 \tag{2.18}$$

With Eqs. (2.14), (2.16) and (2.17) the time-rate of the Gibbs free energy can be written as[2]

$$\rho\dot{g} = -\mathbf{E}\cdot\dot{\mathbf{T}} - \rho s\dot{\theta} + \rho\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k. \tag{2.19}$$

Inserting this relation in combination with the potential relation (2.17) for the specific entropy into the first law of thermodynamics in the form of (2.4), we obtain

$$\rho\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k = \rho\theta\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial g}{\partial\theta}\right) - \mathrm{div}(\vec{q}) + \rho r \tag{2.20}$$

or

$$\rho\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k = \rho\theta\left(\frac{\partial^2 g}{\partial\theta\partial\mathbf{T}}\cdot\dot{\mathbf{T}} + \frac{\partial^2 g}{\partial\theta^2}\dot{\theta} + \sum_{k=1}^{n}\frac{\partial^2 g}{\partial\theta\partial\alpha_k}\dot{\alpha}_k\right) - \mathrm{div}(\vec{q}) + \rho r. \tag{2.21}$$

Rearranging the terms leads finally to

$$-\rho\theta\frac{\partial^2 g}{\partial\theta^2}\dot{\theta} + \rho\sum_{k=1}^{n}\left(\frac{\partial g}{\partial\alpha_k} - \theta\frac{\partial^2 g}{\partial\theta\partial\alpha_k}\right)\dot{\alpha}_k = \rho\theta\frac{\partial^2 g}{\partial\theta\partial\mathbf{T}}\cdot\dot{\mathbf{T}} - \mathrm{div}(\vec{q}) + \rho r. \tag{2.22}$$

To compare this result with the original formulation (1.10) we consider the definition (2.2) in combination with the potential relation (2.17) and obtain

$$h = g - \theta\frac{\partial g}{\partial\theta}. \tag{2.23}$$

This expression leads to the interpretation of the factor $-\theta\partial^2 g/\partial\theta^2$ in Eq. (2.22) as heat capacity at constant stress,

$$c_P(\mathbf{T}, \theta, \alpha_1, \ldots, \alpha_n) = \frac{\partial h}{\partial\theta} = -\theta\frac{\partial^2 g}{\partial\theta^2}, \tag{2.24}$$

and to the following reformulation of the parenthesized term in Eq. (2.22):

$$\frac{\partial g}{\partial\alpha_k} - \theta\frac{\partial^2 g}{\partial\theta\partial\alpha_k} = \frac{\partial}{\partial\alpha_k}\left(g - \theta\frac{\partial g}{\partial\theta}\right) = \frac{\partial}{\partial\alpha_k}(g + \theta s) = \frac{\partial h}{\partial\alpha_k} \tag{2.25}$$

Assuming a constant state of stress, i.e. $\dot{\mathbf{T}} = \mathbf{0}$, and no volume-distributed heat supply $r = 0$ and carrying out the same

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[2] If the partial derivatives of the Gibbs free energy are interpreted as chemical potentials and the internal variables as phase fractions, the corresponding form of the Gibbs-Duhem equation can be derived from Eq. (2.19).

argumentation which led from Eq. (1.4) to Eq. (1.10), Eq. (2.22) can be written as:

$$-\theta\frac{\partial^2 g}{\partial\theta^2}\dot{\theta}+\sum_{k=1}^{n}\left(\frac{\partial g}{\partial\alpha_k}-\theta\frac{\partial^2 g}{\partial\theta\partial\alpha_k}\right)f_k=\frac{P_{\mathrm{DSC}}}{\Delta m} \tag{2.26}$$

This is the fundamental calorimetric equation formulated with the specific Gibbs free energy $g(\mathbf{T},\theta,\alpha_1,\ldots,\alpha_n)$ as thermodynamic potential. It should be remarked that this result can be derived more directly from Eq. (1.10) by introducing the affinities

$$A_k=-\frac{\partial g}{\partial\alpha_k}\ \text{in combination with}\ \frac{\partial g}{\partial\alpha_k}=\frac{\partial h}{\partial\alpha_k}-\theta\frac{\partial s}{\partial\alpha_k}. \tag{2.27}$$

The advantage of the formulation with the Gibbs free energy is that a sufficient condition (2.18) for the compatibility of the evolution equations (1.8) with the second law of thermodynamics can be specified.

For the considerations in the next section and the sake of clearness we introduce an index-free notation. To this end, we define column vectors

$$\underline{\alpha}=(\alpha_1,\ldots,\alpha_n)^{\mathrm{T}},\quad \underline{f}=(f_1,\ldots,f_n)^{\mathrm{T}}, \tag{2.28}$$

$$\frac{\partial g}{\partial\underline{\alpha}}=\left(\frac{\partial g}{\partial\alpha_1},\ldots,\frac{\partial g}{\partial\alpha_n}\right)^{\mathrm{T}} \tag{2.29}$$

in combination with a scalar product

$$\frac{\partial g}{\partial\underline{\alpha}}\cdot\dot{\underline{\alpha}}=\sum_{k=1}^{n}\frac{\partial g}{\partial\alpha_k}\dot{\alpha}_k. \tag{2.30}$$

In order to distinguish between physical vectors like the heat flux $\vec{q}$ and the column vector of the internal variables, for example, we introduced the notation $\underline{\alpha}$ instead of $\vec{\alpha}$. With these definitions in mind, the set of equations (2.26), (1.8) and (2.18) can be rewritten as follows:

Calorimetric equation:

$$-\theta\frac{\partial^2 g}{\partial\theta^2}\dot{\theta}+\left(\frac{\partial g}{\partial\underline{\alpha}}-\theta\frac{\partial^2 g}{\partial\theta\partial\underline{\alpha}}\right)\cdot\dot{\underline{\alpha}}=\frac{P_{\mathrm{DSC}}}{\Delta m} \tag{2.31}$$

Evolution of internal variables:

$$\dot{\underline{\alpha}}=\underline{f}(\mathbf{T},\theta,\underline{\alpha}) \tag{2.32}$$

Thermodynamic compatibility:

$$\rho\theta\gamma=-\rho\frac{\partial g}{\partial\underline{\alpha}}\cdot\dot{\underline{\alpha}}-\frac{\vec{q}\cdot\mathrm{grad}\theta}{\theta}\geq 0 \tag{2.33}$$

Comment: The second law of thermodynamics in the form of Eq. (2.33) states that the entropy production which is the sum of two contributions has to be non-negative for arbitrary thermomechanical processes. If we consider that both the Gibbs free energy g and the $\dot{\underline{\alpha}}$ are independent on grad θ and assume a special situation with $\mathrm{grad}\theta=\vec{0}$ then Eq. (2.33) leads to

$$\rho\theta\gamma_{\mathrm{int}}=-\rho\frac{\partial g(\mathbf{T},\theta,\underline{\alpha})}{\partial\underline{\alpha}}\cdot\dot{\underline{\alpha}}\geq 0. \tag{2.34}$$

This consequence states, that the entropy production γ_{int} of the internal state variables alone, i.e. without temperature gradient, has also to be non-negative. Taking Eq. (2.34) in combination with Eq. (2.19) into account and assuming a process with $\dot{\theta}=0$ and $\dot{\mathbf{T}}=\mathbf{0}$ we obtain $\dot{g}\leq 0$. This demonstrates that the Gibbs free energy approaches a minimum in the thermodynamic state of equilibrium.

3. Constitutive model

The constitutive model to be developed in this section is formulated to represent the material behaviour in the vicinity of the thermodynamic state of equilibrium. The thermodynamic state of equilibrium corresponds to constant values of the external and internal state variables. Its vicinity is defined by sufficiently small changes in both the temperature θ and the internal variables $\underline{\alpha}$. Changes in pressure or stress are not considered in our study.

To formulate the constitutive theory, we postulate that the equilibrium state of the materials' microstructure at constant stress $\mathbf{T}=-p\mathbf{1}$ and temperature θ_0 is represented by a constant internal variable vector $\underline{\alpha}_0$. It depends on both stress and temperature and is the equilibrium solution of the evolution equations (2.32):

$$\underline{0}=\underline{f}(\mathbf{T},\theta_0,\underline{\alpha}_0)\quad\Leftrightarrow\quad\underline{\alpha}_0=\underline{\varphi}(\mathbf{T},\theta_0) \tag{3.1}$$

The Gibbs free energy g_0 belonging to this state of equilibrium is given by the expression

$$g_0=g(\mathbf{T},\theta_0,\underline{\alpha}_0). \tag{3.2}$$

Now, we prescribe a sufficiently small time-dependent temperature perturbation $\vartheta\ (t)$ such that the current temperature can be expressed as

$$\theta(t)=\theta_0+\vartheta(t)\,\text{with}\,|\vartheta(t)|\ll\theta_0. \tag{3.3}$$

The temperature change $\vartheta\ (t)$ leads to time-dependent changes $\underline{\delta}(t)$ in the internal variables:

$$\underline{\alpha}(t)=\underline{\alpha}_0+\underline{\delta}(t) \tag{3.4}$$

To model the resulting change in the Gibbs free energy $g(\mathbf{T},\theta_0+\vartheta,\underline{\alpha}_0+\underline{\delta})$ we introduce its Taylor approximation up to the second order:

$$g(\mathbf{T},\theta_0+\vartheta,\underline{\alpha}_0+\underline{\delta})=g_0+a\vartheta+\frac{1}{2}b\vartheta^2+\underline{c}\cdot\underline{\delta}+\frac{1}{2}(\underline{\underline{d}}\underline{\delta})\cdot\underline{\delta}+\underline{e}\cdot\underline{\delta}\vartheta \tag{3.5}$$

The cross-coupling term $\underline{e}\cdot\underline{\delta}\vartheta$ in Eq. (3.5) between the changes in the temperature perturbation and the internal variables has been introduced quite formally, i.e. without physical motivation. But later in this paper we demonstrate, that exactly this term is responsible for the frequency dependence of the specific heat. In a different notation Eq. (3.5) can be rewritten as

$$g(\mathbf{T},\theta_0+\vartheta,\underline{\alpha}_0+\underline{\delta})$$
$$=g_0+\begin{bmatrix}c_1\\ \vdots\\ c_n\\ a\end{bmatrix}\begin{bmatrix}\delta_1\\ \vdots\\ \delta_n\\ \vartheta\end{bmatrix}+\frac{1}{2}\begin{bmatrix}\delta_1\\ \vdots\\ \delta_n\\ \vartheta\end{bmatrix}\begin{bmatrix}d_{11}&\cdots&d_{1n}&e_1\\ \vdots&\ddots&\vdots&\vdots\\ d_{n1}&\cdots&d_{nn}&e_n\\ e_1&\cdots&e_n&b\end{bmatrix}\begin{bmatrix}\delta_1\\ \vdots\\ \delta_n\\ \vartheta\end{bmatrix}. \tag{3.6}$$

The quantities $\underline{c}$ and $\underline{e}$ are column vectors of dimension n containing material parameters, g_0, a and b are scalar parameters and $\underline{\underline{d}}$ is a matrix containing $n\times n$ material constants. In general, the Taylor coefficients g_0, a, b, $\underline{c}$, $\underline{\underline{d}}$, $\underline{e}$ depend on $\mathbf{T}$ and θ_0. Since the matrix in Eq. (3.6) is the symmetric Hessian-matrix of g we conclude

$$\underline{\underline{d}}=\underline{\underline{d}}^{T}. \tag{3.7}$$

The assumption that the Gibbs free energy should grow when the internal variables change from their equilibrium values $\underline{\delta}_0=\underline{0}$ to $\underline{\delta}(t)\neq\underline{0}$ leads to the positive definiteness of $\underline{\underline{d}}$:

$$\underline{\delta}\cdot(\underline{\underline{d}}\underline{\delta})>0 \tag{3.8}$$

In this case, the inverse matrix

$$\underline{\underline{d}}^{-1}\ \text{exists and has the property}\ \underline{\delta}\cdot(\underline{\underline{d}}^{-1}\underline{\delta})>0. \tag{3.9}$$

To attribute the material constants of the specific Gibbs free energy (3.5) to physical material properties we consider Eq. (2.24) and calculate the specific heat:

$$c_P(\vartheta, \underline{\delta}) = -\theta \frac{\partial^2 g}{\partial \vartheta^2} = -(\theta_0 + \vartheta) b = -b\theta_0 - \frac{\vartheta}{\theta_0} b\theta_0 \tag{3.10}$$

We recognize that c_P depends on temperature, but not on the internal variables. If the change in the temperature is zero we obtain $c_P(0, \underline{\delta}) = -b\theta_0$ which motivates the following definition:

$$-b\theta_0 =: c_{P0} \quad \Leftrightarrow \quad b = -\frac{c_{P0}}{\theta_0} \tag{3.11}$$

Based on this, Eq. (3.10) can be written as

$$c_P = \left(1 + \frac{\vartheta}{\theta_0}\right) c_{P0}. \tag{3.12}$$

Now, we consider Eq. (2.17) and calculate the specific entropy from Eq. (3.5):

$$s(\vartheta, \underline{\delta}) = -\frac{\partial g}{\partial \vartheta} = -(a + b\vartheta + \underline{e} \cdot \underline{\delta}) \tag{3.13}$$

It depends on both the temperature perturbation and the changes in the internal state variables. Interpreting the internal variables as order parameters or as quantities describing the current state of the microstructure, the dependence of the entropy on $\underline{\delta}$ becomes obvious. In the case of $\vartheta = 0$ and $\underline{\delta} = \underline{0}$ we have

$$s(0, \underline{0}) = -a =: s_0. \tag{3.14}$$

This leads to the interpretation of the material constant $-a$ as the entropy s_0 in the reference state at $\theta = \theta_0$ and $\underline{\alpha} = \underline{\alpha}_0$.

To satisfy Eq. (2.33), the sum of the two contributions to the entropy production has to be non-negative. Since the Gibbs free energy and the rates of the internal variables are independent of grad θ, we concluded that the entropy production of the internal variables has to be non-negative. In order to formulate the evolution equations for the internal variables such that Eq. (2.34) is satisfied, we consider Eq. (3.5), calculate the affinities

$$-\frac{\partial g}{\partial \underline{\delta}} = -(\underline{c} + \underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta) \tag{3.15}$$

and obtain:

$$\rho\theta_0\gamma_{\text{int}} = -\frac{\partial g}{\partial \underline{\delta}} \cdot \dot{\underline{\delta}} = -(\underline{c} + \underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta) \cdot \dot{\underline{\delta}}. \tag{3.16}$$

In order to guarantee $-(\partial g/\partial \underline{\delta}) \cdot \dot{\underline{\delta}} \geq 0$ for arbitrary thermomechanical processes we define

$$\dot{\underline{\delta}}(t) := -\underline{\underline{A}}(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta) \text{ with } \underline{\delta}(0) = \underline{0} \tag{3.17}$$

for the temporal evolution of the internal variables (cf. Eq. (2.32)). To make sure that the temporal changes in the internal variables are zero when the material is in its reference state at $\vartheta = 0$ and $\underline{\delta} = \underline{0}$, the parameter vector $\underline{c}$ has to be zero. The $n \times n$ matrix $\underline{\underline{A}}$ has to be positive definite such that the corresponding entropy production is non-negative:

$$-\frac{\partial g}{\partial \underline{\delta}} \cdot \dot{\underline{\delta}} = (\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta) \cdot (\underline{\underline{A}}(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta)) \geq 0 \tag{3.18}$$

The driving force for the changes in the internal variables is the temperature perturbation such that the system (3.17) of linear differential equations has the following properties:

- The general solution of Eq. (3.17) for arbitrary temperature perturbations is given by the following convolution integral, where exp(...) is the matrix exponential function:

  $$\underline{\delta}(t) = -\int_0^t \exp(-\underline{\underline{Ad}}(t - s))\underline{\underline{A}}\underline{e}\vartheta(s)\mathrm{d}s \tag{3.19}$$

  The internal variable vector $\underline{\delta}$ is a linear functional of the history of the temperature perturbation with fading memory properties: if an arbitrary temperature perturbation $\vartheta(s)$ is switched-off for $s \geq t_0$, the internal variables relax to their initial values since Eq. (3.19) leads for $t \geq t_0$ to $\lim_{t\to\infty} \underline{\delta}(t) = \underline{0}$.
- If the temperature perturbation is zero, then Eq. (3.19) leads to $\underline{\delta}(t) \equiv \underline{0}$, i.e. the internal variables do not evolve in this case. The requirement of asymptotic stability of this solution demands the matrix $\underline{\underline{Ad}}$ to be positive definite:

  $$\underline{\delta} \cdot (\underline{\underline{Ad}})\underline{\delta} > 0 \quad \Rightarrow \quad (\underline{\underline{Ad}})^{-1} \quad \text{exists} \tag{3.20}$$

  The reciprocal eigenvalues of the matrix $\underline{\underline{Ad}}$ are the relaxation times of the internal variables and can be interpreted as time constants of the materials' microstructure. The distinction, whether a temperature change is slow or fast for a given material depends on the ratio between the reciprocal eigenvalues of the matrix $\underline{\underline{Ad}}$ and the characteristic time constants of the temperature process.
- Assuming infinitely slow temperature perturbations, we are close to equilibrium such that the rate terms $\dot{\vartheta}$ and $\dot{\underline{\delta}}$ can be neglected in the equations. Then, Eq. (3.17) leads to $\underline{0} = \underline{\underline{A}}(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta)$ and finally to $\underline{\delta} = -(\underline{\underline{d}}^{-1}\underline{e})\vartheta$, i.e. the changes in the internal variables depend linearly on the temperature perturbation. The physical interpretation is that the microstructure of the material follows the temperature change in a reversible manner without any delay. In this case, the entropy which is given by (3.13) or (3.24) changes due to both the temperature variation and the variation in the internal variables.
- In the case of infinitely fast temperature changes, the terms containing ϑ and $\underline{\delta}$ can be neglected in comparison with the rate terms. Then, Eq. (3.17) leads to $\dot{\underline{\delta}} = \underline{0}$ or with the initial condition $\underline{\delta}(0) = \underline{0}$ to $\underline{\delta}(t) \equiv \underline{0}$, i.e. the internal state variables are frozen. The physical interpretation of this consequence is that the microstructure does not follow the temperature change. In this case, the entropy (3.13) or (3.24) only changes due to the temperature variation.

Using these results, the calorimetric equation corresponding to Eq. (2.31) can easily be derived. To this end, the expression

$$\left(\frac{\partial g}{\partial \underline{\delta}} - \theta \frac{\partial^2 g}{\partial \theta \partial \underline{\delta}}\right) \cdot \dot{\underline{\delta}} = -(\underline{\underline{d}}\underline{\delta} - \theta_0 \underline{e}) \cdot (\underline{\underline{A}}(\underline{\underline{d}}\underline{\delta} + \underline{e}\vartheta)) \tag{3.21}$$

is expanded and written as

$$\begin{aligned}\left(\frac{\partial g}{\partial \underline{\delta}} - \theta \frac{\partial^2 g}{\partial \theta \partial \underline{\delta}}\right) \cdot \dot{\underline{\delta}} = {} & -\underline{\delta} \cdot [(\underline{\underline{dAd}})\underline{\delta}] - \underline{\delta} \cdot [(\underline{\underline{dA}})\underline{e}]\vartheta + \theta_0 \underline{e} \cdot (\underline{\underline{A}}\underline{e})\vartheta \\ & + \theta_0 \underline{e} \cdot [(\underline{\underline{Ad}})\underline{\delta}].\end{aligned} \tag{3.22}$$

After these reformulations and considerations we obtain the final versions of the Gibbs free energy, the entropy, the heat capacity, the evolution equations for the internal state variables and the calorimetric equation:

Gibbs free energy:

$$g = g_0 - s_0\vartheta - \frac{c_{P0}}{2\theta_0}\vartheta^2 + \frac{1}{2}(\underline{\underline{d}}\underline{\delta}) \cdot \underline{\delta} + \underline{e} \cdot \underline{\delta}\vartheta \tag{3.23}$$

Entropy:

$$s = s_0 + \frac{c_{P0}}{\theta_0}\vartheta - \underline{e} \cdot \underline{\delta} \tag{3.24}$$

Heat capacity:

$$c_P = \left(1 + \frac{\vartheta}{\theta_0}\right) c_{P0} \tag{3.25}$$

Evolution of internal variables:

$$\dot{\underline{\delta}} = -\underline{\underline{A}}(\underline{\underline{d}}\,\underline{\delta} + \underline{e}\vartheta) \tag{3.26}$$

DCR:

$$c_{P0}\dot{\vartheta} + \theta_0(\underline{e}\cdot(\underline{\underline{A}}\,\underline{e})\vartheta + \underline{e}\cdot[(\underline{\underline{Ad}})\underline{\delta}]) + c_{P0}\frac{\vartheta}{\theta_0}\dot{\vartheta} - \underline{\delta}\cdot[(\underline{\underline{dAd}})\underline{\delta}] - \underline{\delta}\cdot[(\underline{\underline{dA}})\underline{e}]\vartheta = \frac{P_{\mathrm{DSC}}}{\Delta m} \tag{3.27}$$

These equations define the theory which can be applied to represent the dynamic calorimetric response (DCR) of a given material due to a temperature perturbation in the vicinity of the thermodynamic state of equilibrium. The material parameters are given by the scalars g_0, s_0, c_{P0}, the n-dimensional parameter column $\underline{e}$, the symmetric and positive definite $n\times n$ matrix $\underline{\underline{d}}$ and the positive definite $n\times n$ matrix $\underline{\underline{A}}$. As we see, the first three terms on the left-hand side of Eq. (3.27) depend linearly on ϑ, its time-rate or $\underline{\delta}$. When a harmonic temperature excitation is prescribed, these terms oscillate with the same frequency as the temperature and determine the frequency dependence of the specific heat. The three other terms depend on products between ϑ, its time-rate or $\underline{\delta}$ and lead to a contribution to the dynamic calorimetric response which oscillates with the double frequency. If the material parameter vector $\underline{e}$ is zero, the cross-coupling term in the Gibbs free energy vanishes, the contribution of the internal state variables to the entropy also vanishes, the internal variables remain zero and Eq. (3.27) reduces to $c_{P0}\dot{\vartheta} + (c_{P0}/\theta_0)\vartheta\dot{\vartheta} = P_{\mathrm{DSC}}/\Delta m$. The term containing the product $\vartheta\dot{\vartheta}$ is due to the temperature dependence of the heat capacity.

4. Evaluation for harmonic temperature changes

To analyse the Eqs. (3.26) and (3.27) for harmonic temperature changes and to derive an expression for the complex heat capacity we prescribe a temperature excitation in the form of

$$\vartheta(t) = \hat{\vartheta}e^{i\omega t}. \tag{4.1}$$

The parameter ω is the angular frequency, $i=\sqrt{-1}$ the imaginary unit and $\hat{\vartheta}$ the amplitude of the temperature excitation. Since Eq. (3.26) is a system of linear differential equations, the stationary response of the internal state variables can be represented as

$$\underline{\delta} = \hat{\underline{\delta}}(\omega)e^{i\omega t}. \tag{4.2}$$

The complex amplitudes $\hat{\underline{\delta}}(\omega)$ of the internal variables describe the magnitude and the phase and depend on the frequency of the temperature process. Inserting Eqs. (4.1) and (4.2) into Eq. (3.26) leads to the intermediate result

$$i\omega\hat{\underline{\delta}} = -\underline{\underline{A}}(\underline{\underline{d}}\,\hat{\underline{\delta}} + \underline{e}\hat{\vartheta}). \tag{4.3}$$

Introducing the $n\times n$ unit matrix $\underline{\underline{1}}$ and defining the frequency-dependent transfer function

$$\hat{\underline{\Delta}}(\omega) = -(i\omega\underline{\underline{1}} + \underline{\underline{Ad}})^{-1}\underline{\underline{A}}\,\underline{e} \tag{4.4}$$

we obtain the following relation for the amplitudes of the internal variables:

$$\hat{\underline{\delta}}(\omega) = \hat{\underline{\Delta}}(\omega)\hat{\vartheta} \tag{4.5}$$

To calculate the dynamic calorimetric response we insert at first Eqs. (4.1) and (4.2) into Eq. (3.27):

$$i\omega c_{P0}\hat{\vartheta}e^{i\omega t} + i\omega\frac{\hat{\vartheta}^2}{\theta_0}c_{P0}e^{2i\omega t} + \theta_0(\underline{e}\cdot(\underline{\underline{A}}\,\underline{e})\hat{\vartheta}e^{i\omega t} + \underline{e}\cdot[(\underline{\underline{Ad}})\hat{\underline{\delta}}]e^{i\omega t}) + - \hat{\underline{\delta}}\cdot[(\underline{\underline{dAd}})\hat{\underline{\delta}}]e^{2i\omega t} - \hat{\underline{\delta}}\cdot[(\underline{\underline{dA}})\underline{e}]\hat{\vartheta}e^{2i\omega t} = \frac{P_{\mathrm{DSC}}}{\Delta m} \tag{4.6}$$

Replacing the internal state variable amplitudes $\hat{\underline{\delta}}(\omega)$ by (4.5) and reorganizing the terms we obtain the following intermediate result:

$$\left\{c_{P0} + \frac{\theta_0}{i\omega}(\underline{e}\cdot(\underline{\underline{A}}\,\underline{e}) + \underline{e}\cdot[\underline{\underline{Ad}}\,\hat{\underline{\Delta}}])\right\}i\omega\hat{\vartheta}e^{i\omega t} + \left\{\frac{i\omega c_{P0}}{\theta_0} - \hat{\underline{\Delta}}\cdot[\underline{\underline{dAd}}\,\hat{\underline{\Delta}} + \underline{\underline{dA}}\,\underline{e}]\right\}\hat{\vartheta}^2e^{2i\omega t} = \frac{P_{\mathrm{DSC}}}{\Delta m}. \tag{4.7}$$

Multiplying the definition (4.4) of the transfer function $\hat{\underline{\Delta}}(\omega)$ with the matrix $(i\omega\underline{\underline{1}} + \underline{\underline{Ad}})$ and rearranging the terms, we obtain

$$\underline{\underline{A}}(\underline{e} + \underline{\underline{d}}\,\hat{\underline{\Delta}}(\omega)) = -i\omega\hat{\underline{\Delta}}(\omega) \tag{4.8}$$

and after a short calculation the final expression for the dynamic calorimetric response:

$$[c_{P0} - \theta_0\underline{e}\cdot\hat{\underline{\Delta}}(\omega)]i\omega\hat{\vartheta}e^{i\omega t} + i\omega\left[\frac{c_{P0}}{\theta_0} + \hat{\underline{\Delta}}(\omega)\cdot\underline{\underline{d}}\,\hat{\underline{\Delta}}(\omega)\right]\hat{\vartheta}^2e^{2i\omega t} = \frac{P_{\mathrm{DSC}}}{\Delta m} \tag{4.9}$$

We see that there occur two frequencies in the dynamic calorimetric response: one term oscillates with the frequency ω and the other with its double. The 2ω-term is small because it is multiplied with the square $\hat{\vartheta}^2$ of the temperature amplitude. In the comprehensive article [18], higher-order terms in TMDSC responses as well as their different reasons are analysed. Since the expression $i\omega\hat{\vartheta}e^{i\omega t}$ in Eq. (4.9) is the rate of the temperature, its coefficient can be interpreted as a complex frequency-dependent heat capacity:

$$\hat{c}_P(\omega) = c_{P0} - \theta_0\underline{e}\cdot\hat{\underline{\Delta}}(\omega) \tag{4.10}$$

Taking Eq. (4.4) into account, Eq. (4.10) reads is in a more explicit form

$$\hat{c}_P(\omega) = c_{P0} + \theta_0\underline{e}\cdot(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1}\underline{\underline{A}}\,\underline{e}. \tag{4.11}$$

In addition to the constant c_{P0} which was introduced by Eqs. (3.11), (3.23) or (3.25) a frequency-dependent term occurs which is proportional to the transfer function of the internal state variables. From a physical point of view, this contribution is determined by temperature-induced dynamic changes in the microstructure of the material. If the material parameter vector $\underline{e}$ equals zero, the cross-coupling term in the Gibbs free energy (3.23) vanishes and the internal variable vector $\underline{\delta}$, or the microstructure, remains uninfluenced by the temperature perturbation (see Eqs. (3.26) and (4.5) or (4.4)). In this case, we obtain from Eq. (4.11) the relation $\hat{c}_P(\omega) = c_{P0}$, i.e. the heat capacity is a real number and is frequency-independent. In the case of $\underline{e} \neq \underline{0}$, the internal variables vary with the same frequency as the temperature excitation but with a frequency-dependent amplitude and phase. Since these microstructural rearrangements absorb and release energy, the specific heat of the material is influenced (cf. [7,29,30]).

To compare these results with experimental observations from literature (see refs. [1] or [19]) we evaluate Eq. (4.11) for low and high frequencies.

4.1. Low-frequent behaviour

In order to investigate the low-frequent behaviour of the complex heat capacity we take a look at Eq. (4.11), consider the positive definiteness of the matrices $\underline{\underline{A}}$ and $\underline{\underline{d}}$, set $\omega = 0$ and obtain

$$\hat{c}_P(0) = c_{P0} + \theta_0\underline{e}\cdot(\underline{\underline{A}}\,\underline{\underline{d}})^{-1}\underline{\underline{A}}\,\underline{e} \tag{4.12}$$

or

$$\hat{c}_P(0) = c_{P0} + \theta_0\underline{e}\cdot(\underline{\underline{d}}^{-1}\underline{e}). \tag{4.13}$$

The additional term on the right-hand side of Eq. (4.13) is non-negative because $\underline{\underline{d}}$ and its inverse are positive definite matrices (see Eqs. (3.8) and (3.9)). In order to interpret this result, we calculate the low-frequent behaviour of the amplitudes of the internal variables. Relations (4.4) and (4.5) together with $\omega = 0$ lead to

$$\hat{\underline{\delta}}(0) = -\underline{\underline{d}}^{-1}\underline{e}\hat{\vartheta}. \tag{4.14}$$

which corresponds to the solution of Eq. (3.26) for infinitely slow processes. This result exhibits that the amplitude of the internal state variable vector becomes constant and different from zero when the frequency of the dynamic temperature excitation is sufficiently small. In this case, the microstructure follows the dynamic changes in temperature.

4.2. *High-frequent behaviour*

To study the high-frequent behaviour of the complex heat capacity we reformulate Eq. (4.11) as

$$\hat{c}_P(\omega) = c_{P0} + \frac{\theta_0}{i\omega}\underline{e}\cdot\left(\underline{\underline{1}} + \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\underline{e}. \tag{4.15}$$

Since the assumption of high frequencies implies $||(1/i\omega)\underline{\underline{A}}\,\underline{\underline{d}}|| \ll 1$ we apply the approximation

$$\left(\underline{\underline{1}} + \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1} \approx \underline{\underline{1}} - \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}} \tag{4.16}$$

which leads to the intermediate result

$$\hat{c}_P(\omega) = c_{P0} + \frac{\theta_0}{i\omega}\underline{e}\cdot\left(\underline{\underline{1}} - \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}}\right)\underline{\underline{A}}\underline{e}. \tag{4.17}$$

Carrying out the limit transition $\omega \to \infty$ we obtain

$$\hat{c}_P(\infty) = c_{P0}. \tag{4.18}$$

In the case of high-frequent temperature processes, the complex heat capacity is given by the material constant c_{P0}. For the sake of completeness, we also calculate the dynamic amplitudes of the internal variables. To this end, we factor out the term $1/i\omega$ in Eqs. (4.4) and (4.5):

$$\hat{\underline{\delta}}(\omega) = -\frac{1}{i\omega}\left(\underline{\underline{1}} + \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}}\right)^{-1}\underline{\underline{A}}\underline{e}\hat{\vartheta} \tag{4.19}$$

Application of the approximation (4.16) leads to

$$\hat{\underline{\delta}}(\omega) = -\frac{1}{i\omega}\left(\underline{\underline{1}} - \frac{1}{i\omega}\underline{\underline{A}}\,\underline{\underline{d}}\right)\underline{\underline{A}}\underline{e}\hat{\vartheta} \tag{4.20}$$

and after the limit transition $\omega \to \infty$ to

$$\hat{\underline{\delta}}(\infty) = \underline{0}. \tag{4.21}$$

In the case of high-frequent temperature changes, the internal state variables are frozen and do not change. The frequency of the temperature process is too large.

4.3. *Interpretation of the imaginary part of the complex heat capacity*

In order to interpret the complex specific heat as done, for example, in refs. [12,29,30] we reformulate Eq. (4.11) using the identity

$$\begin{aligned}(i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1} &= (i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1}(-i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1}(-i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})\\ &= (\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}(-i\omega\underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})\end{aligned} \tag{4.22}$$

and obtain the additive split of $\hat{c}_P(\omega)$ the sum of real and imaginary parts:

$$\begin{aligned}\hat{c}_P(\omega) \;&=\; \mathrm{Re}(\hat{c}_P) - i\mathrm{Im}(\hat{c}_P)\\ &\mathrm{Re}(\hat{c}_P) = c_{P0} + \theta_0\underline{e}\cdot(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\,\underline{\underline{d}}\,\underline{\underline{A}}\underline{e}\\ &\mathrm{Im}(\hat{c}_P) = \omega\theta_0\underline{e}\cdot(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\underline{e}\end{aligned} \tag{4.23}$$

The current entropy production $\rho\gamma_{\mathrm{int}}(t)$ due to temporal changes in the internal variables or rearrangements of the microstructure can be calculated by Eq. (3.18) or with Eq. (3.26) by

$$\rho\theta_0\gamma_{\mathrm{int}} = -\frac{\partial g}{\partial\underline{\delta}}\cdot\dot{\underline{\delta}} = \dot{\underline{\delta}}\cdot(\underline{\underline{A}}^{-1}\dot{\underline{\delta}}). \tag{4.24}$$

The total amount of entropy ΔS_{cycl} generated during a temperature cycle can be calculated by integration:

$$\theta_0\Delta S_{\mathrm{cycl}} = \theta_0\rho\int_0^{2\pi/\omega}\gamma_{\mathrm{int}}(t)\mathrm{d}t = \int_0^{2\pi/\omega}\dot{\underline{\delta}}(t)\cdot\underline{\underline{A}}^{-1}\dot{\underline{\delta}}(t)\mathrm{d}t \tag{4.25}$$

The rate of the internal state variable vector can be determined, for example, by solving Eq. (3.26) for a sinusoidal temperature perturbation:

$$\vartheta(t) = \hat{\vartheta}\sin(\omega t) \tag{4.26}$$

Inserting the ansatz for the internal state variable vector

$$\underline{\delta}(t) = \underline{\delta}_1(\omega)\sin(\omega t) + \underline{\delta}_2(\omega)\cos(\omega t) \tag{4.27}$$

into the evolution equation (3.26) leads to

$$(\underline{\underline{A}}\,\underline{\underline{d}}\underline{\delta}_2 + \omega\underline{\delta}_1)\cos(\omega t) = (\omega\underline{\delta}_2 - \underline{\underline{A}}\,\underline{\underline{d}}\underline{\delta}_1 - \underline{\underline{A}}\underline{e}\hat{\vartheta})\sin(\omega t). \tag{4.28}$$

Since the coefficients of the sine and cosine functions have to vanish, two linear equations for $\underline{\delta}_1$ and $\underline{\delta}_2$ are obtained. Solving these equations leads to

$$\underline{\delta}_1 = -\underline{\underline{A}}\,\underline{\underline{d}}(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\underline{e}\hat{\vartheta} \text{ and } \underline{\delta}_2 = \omega(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\underline{e}\hat{\vartheta} \tag{4.29}$$

and finally to the stationary solution

$$\underline{\delta}(t) = (\omega\underline{\underline{1}}\cos(\omega t) - \underline{\underline{A}}\,\underline{\underline{d}}\sin(\omega t))(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\underline{e}\hat{\vartheta} \tag{4.30}$$

for internal variable vector. Differentiating Eq. (4.30) with respect to time and application of the matrix-vector calculus leads to:

$$\begin{aligned}\dot{\underline{\delta}}\cdot\underline{\underline{A}}^{-1}\dot{\underline{\delta}} &= \omega^2(\omega^2\underline{\underline{A}}^{-1}\sin^2(\omega t) + 2\omega\underline{\underline{d}}\sin(\omega t)\cos(\omega t)\\ &\quad + \underline{\underline{d}}\,\underline{\underline{A}}\,\underline{\underline{d}}\cos^2(\omega t))\underline{x}\cdot\underline{x} \quad \text{with} \quad \underline{x} = (\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)^{-1}\underline{\underline{A}}\underline{e}\hat{\vartheta}\end{aligned} \tag{4.31}$$

Carrying out the integration over one cycle and considering

$$\int_0^{2\pi/\omega}\sin^2(\omega t)\mathrm{d}t = \int_0^{2\pi/\omega}\cos^2(\omega t)\mathrm{d}t = \frac{\pi}{\omega} \text{ and}$$

$$\int_0^{2\pi/\omega}\sin(\omega t)\cos(\omega t)\mathrm{d}t = 0 \tag{4.32}$$

we obtain from Eq. (4.25) together with Eq. (4.31):

$$\begin{aligned}\theta_0\Delta S_{\mathrm{cycl}} &= \pi\omega(\omega^2\underline{\underline{A}}^{-1} + \underline{\underline{d}}\,\underline{\underline{A}}\,\underline{\underline{d}})\underline{x}\cdot\underline{x}\\ &= \pi\omega\underline{\underline{A}}^{-1}(\omega^2\underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2)\underline{x}\cdot\underline{x} = \pi\hat{\vartheta}\omega\underline{e}\cdot\underline{x}\end{aligned} \tag{4.33}$$

Taking the definitions (4.31) of the auxiliary variable $\underline{x}$ and (4.23) of the split of $\hat{c}_P(\omega)$ into real and imaginary parts into account, we obtain the final result:

$$\Delta S_{\text{cycl}} = \pi \frac{\hat{\vartheta}^2}{\theta_0} \omega \underline{e} \cdot \left(\omega^2 \underline{\underline{1}} + (\underline{\underline{A}}\,\underline{\underline{d}})^2\right)^{-1} \underline{\underline{A}}\,\underline{e} = \pi \frac{\hat{\vartheta}^2}{\theta_0^2} Im(\hat{c}_p) \tag{4.34}$$

This simple expression relates the imaginary part of the complex specific heat to the produced entropy during a temperature cycle. It is in accordance with the expression provided by ref. [12].

5. Numerical simulations and discussion

In order to illustrate the properties of the constitutive theory, we assume decoupled evolution equations for the internal state variables such that the matrices in the evolution equations and the Gibbs free energy are diagonal. To this end, the vectors $\underline{e}$ and $\underline{\hat{\delta}}$ and the positive definite diagonal matrices $\underline{\underline{A}}$ and $\underline{\underline{d}}$ are represented as

$$\underline{\underline{A}} = \begin{bmatrix} A_1 & & & \\ & \cdots & & \\ & & \cdots & \\ & & & A_n \end{bmatrix}, \quad \underline{\underline{d}} = \begin{bmatrix} d_1 & & & \\ & \cdots & & \\ & & \cdots & \\ & & & d_n \end{bmatrix},$$

$$\underline{e} = \begin{bmatrix} e_1 \\ \cdots \\ \cdots \\ e_n \end{bmatrix} \quad \text{and} \quad \underline{\hat{\delta}} = \begin{bmatrix} \hat{\delta}_1 \\ \cdots \\ \cdots \\ \hat{\delta}_n \end{bmatrix}. \tag{5.1}$$

Application of the matrix-vector calculus leads to the expressions

$$(i\omega \underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1} \underline{\underline{A}}\,\underline{e} = \begin{bmatrix} \dfrac{A_1 e_1}{i\omega + A_1 d_1} \\ \cdots \\ \cdots \\ \dfrac{A_n e_n}{i\omega + A_n d_n} \end{bmatrix} \tag{5.2}$$

and

$$\underline{e} \cdot [(i\omega \underline{\underline{1}} + \underline{\underline{A}}\,\underline{\underline{d}})^{-1} \underline{\underline{A}}\,\underline{e}] = \sum_{k=1}^{n} \frac{A_k e_k^2}{i\omega + A_k d_k}. \tag{5.3}$$

Inserting Eq. (5.3) into Eq. (4.11) and splitting it into real and imaginary parts yields the expression

$$\hat{c}_P(\omega) = c_{P0} + \theta_0 \sum_{k=1}^{n} \frac{A_k e_k^2}{i\omega + A_k d_k} = \text{Re}(\hat{c}_P) - i\text{Im}(\hat{c}_P) \tag{5.4}$$

for the complex heat capacity with

$$\text{Re}(\hat{c}_P) = c_{P0} + \theta_0 \sum_{k=1}^{n} \frac{e_k^2/d_k}{1 + (\omega/A_k d_k)^2}, \tag{5.5}$$

$$\text{Im}\left(\hat{c}_P\right) = \theta_0 \sum_{k=1}^{n} \frac{\left(\omega/A_k d_k\right) e_k^2/d_k}{1 + \left(\omega/A_k d_k\right)^2}. \tag{5.6}$$

The real part of the complex heat capacity is a positive and monotonically decreasing function of the angular frequency ω. The imaginary part is also positive but can have several maxima and minima. The frequency-dependent contribution to the complex heat capacity (5.4) has the same structure as the expression proposed in refs. [7,8,29,30] and corresponds to a generalization of it.

The positive numbers $\tau_k = 1/A_k d_k$ in Eqs. (5.5) and (5.6) can be interpreted as characteristic time scales of the corresponding micromechanical processes which are represented by the internal variables. This interpretation becomes more clear if the complex amplitudes $\hat{\delta}_k(\omega)$ of the micromechanical processes are calculated. Using Eqs. (4.4), (4.5) and (5.2) we obtain

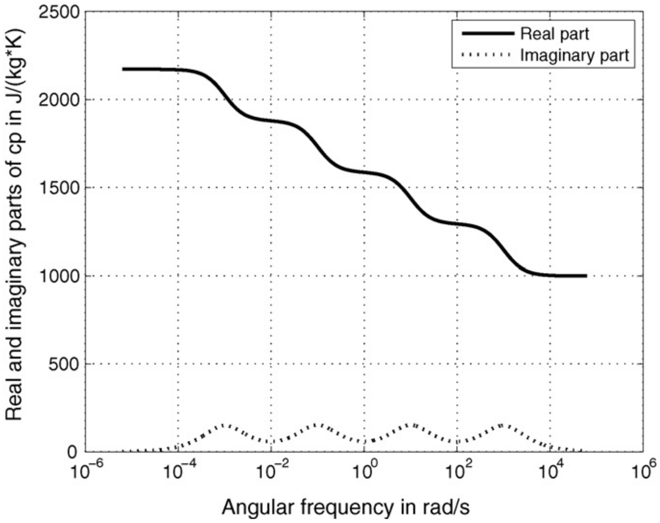

Fig. 1. Real and imaginary parts of the complex heat capacity.

$$\hat{\delta}_k(\omega) = -\frac{A_k e_k}{i\omega + A_k d_k} \hat{\vartheta} = |\hat{\delta}_k| e^{i\varphi_k} \tag{5.7}$$

with

$$|\hat{\delta}_k| = \frac{|e_k/d_k|}{\sqrt{1 + (\omega/A_k d_k)^2}} |\hat{\vartheta}| \quad \text{and} \quad \tan(\varphi_k) = \frac{-\omega}{A_k d_k} \tag{5.8}$$

In the high-frequent case of $\omega/A_k d_k \gg 1$ the amplitude of the corresponding process vanishes and also its contribution to the complex heat capacity (5.4). In the opposite or low-frequent case of $\omega/A_k d_k \ll 1$ the micromechanical process is in phase with the temperature excitation and, thus, contributes to the specific heat capacity.

The frequency-dependent behaviour of the proposed model is illustrated in the following three figures. To highlight the fundamental properties, we took the choice of four internal variables or micromechanical mechanisms with a different and widely spread dynamic behaviour. The material constants are given by the following numerical values:

$$A_1 = A_2 = A_3 = A_4 = 1\,\frac{kg}{Js}, c_{P0} = 10^3\,\frac{J}{kgK}, s_0 = 0, g_0 = 0$$

$$d_1 = 10^3\,\frac{J}{kg}, d_2 = 10^1\,\frac{J}{kg}, d_3 = 10^{-1}\,\frac{J}{kg}, d_4 = 10^{-3}\,\frac{J}{kg}$$

$$e_1 = -10^{3/2}\,\frac{J}{kgK}, e_2 = -10^{1/2}\,\frac{J}{kgK}, e_3 = -10^{-1/2}\,\frac{J}{kgK},$$

$$e_4 = -10^{-3/2}\,\frac{J}{kgK}$$

Fig. 1 visualizes both the monotonically decreasing behaviour of the real part of the complex heat capacity and the maxima and minima of the imaginary part. The material constants were chosen such that the minima of the imaginary part of $\hat{c}_P$ are located at angular frequencies of about 10^{-3} rad/s, 10^{-1} rad/s, 10^{1} rad/s and 10^{3} rad/s. This type of behaviour is in accordance with the experimental data observed in refs. [1] and [19].

In Figs. 3 and 4 of [19] there are some indications that there are possibly two mechanisms contributing to the complex specific heat of glycerol. In Fig. 3 of [1], propylene glycol has been studied. The transition region of the complex heat capacity from the low- to

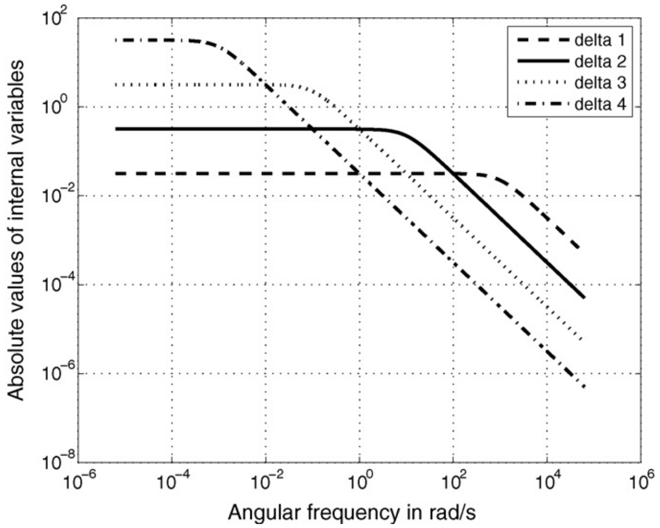

Fig. 2. Absolute values of the four internal variables.

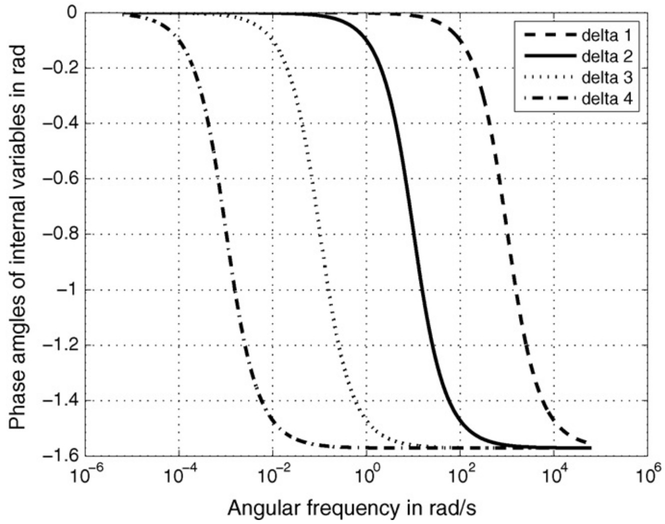

Fig. 3. Phase angles of the four internal variables.

the high-frequent level is about two or three decades. This broad region suggests that there are also several coexisting mechanisms contributing to the specific heat.

In Figs. 2 and 3, the amplitudes and phase angles of the internal variable amplitudes are plotted against the angular frequency. The characteristic transition frequency of each variable is given by the product $A_k d_k$ of its material parameters.

If the frequency of the temperature process is smaller than the characteristic frequency of the corresponding internal state variable, its amplitude has the maximum, is nearly constant and the phase shift is zero. At essentially higher excitation frequencies, the amplitudes of the internal variables tend asymptotically to zero and the phase shifts to $-\pi/2$ i.e. the internal state variables are frozen. Comparing Figs. 1 and 2, we observe that at frequencies below 10^{-4} rad/s the specific heat has the highest values and is constant since all four internal variable amplitudes are constant and vary in phase with the temperature. Between frequencies of 10^{-4} rad/s and 10^{-2} rad/s the real part of the heat capacity decreases because the amplitude of the first internal state variable or micromechanical process becomes essentially smaller. At about 10^{-2} rad/s the specific heat is constant again because the three other mechanisms have constant amplitudes and change in phase with the temperature process.

6. Conclusions

To represent the frequency-dependent heat capacity which can be measured by TMDSC, we developed a constitutive approach which is based on thermodynamics with internal state variables. Motivated by the external variables prescribed in differential scanning calorimetry, the Gibbs free energy is chosen as appropriate thermodynamic potential. Its canonical independent variables are the stress tensor and the thermodynamic temperature. In order to take the temperature-dependence of the materials' microstructure into account, a finite set of internal state variables is introduced as additional arguments of the Gibbs free energy. The evolution equations for these variables are formulated such that the whole constitutive model is compatible with the second law of thermodynamics in the form of the Clausius–Duhem inequality. To formulate the constitutive model as general as possible, a Taylor approximation of the Gibbs free energy up to second order terms in the temperature and the internal variables was applied. The developed model is valid in a certain neighbourhood of the thermodynamic state of equilibrium.

The substantial results of this paper are expressions in closed form for both the dynamic calorimetric response and the complex heat capacity. The frequency-dependent part of the complex heat capacity is proportional to the transfer function of the internal state variables. According to findings from literature, we have shown that the imaginary part of the specific heat determines the entropy which is produced by the changes in the internal variables during one sinusoidal temperature cycle. The material parameters of the model can be identified by fitting the real and imaginary parts of the frequency-dependent heat capacity to experimental data. An interesting property of our model is that the real part of the complex heat capacity decreases with increasing temperature frequencies. The imaginary part shows several maxima and minima.

From a physical point of view, the heat capacity is frequency-dependent if the material under consideration exhibits reversible temperature-induced changes in its microstructure. In the case of temperature excitations with sufficient high frequencies, the microstructure is frozen such that no additional energy is absorbed or emitted by it when the temperature varies. In the opposite case of sufficiently small temperature frequencies, the microstructure follows the dynamic temperature excitation without delay and an additional amount of energy is absorbed or emitted in order to realize the changes in the microstructure. In the case of intermediate frequencies, the microstructure follows with a frequency-dependent delay or phase shift. In this case, both the imaginary part of the specific heat and the amount of entropy which is generated during a temperature cycle have a local maximum.

The constitutive theory developed in this paper is in accordance with experimental data of the complex heat capacity provided by ref. [1] as well as by ref. [19]. Our theoretical results correspond to a generalization of the fundamental formula for the complex heat capacity derived in refs. [7,8,29].

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