Thermomechanical material modelling based on a hybrid free energy density depending on pressure, isochoric deformation and temperature

CrossMark

A. Lion *, B. Dippel, C. Liebl

Institute of Mechanics, Department of Aerospace Engineering, Universität der Bundeswehr München, D-85577 Neubiberg, Germany

ARTICLE INFO

ABSTRACT

In order to represent temperature-dependent mechanical material properties in a thermomechanical consistent manner it is common practice to start with the definition of a model for the specific Helmholtz free energy. Its canonical independent variables are the Green strain tensor and the temperature. But to represent calorimetric material properties under isobaric conditions, for example the exothermal behaviour of a curing process or the dependence of the specific heat on the temperature history, the temperature and the pressure should be taken as independent variables. Thus, in the field of calorimetry the Gibbs free energy is usually used as thermodynamic potential whereas in continuum mechanics the Helmholtz free energy is normally applied. In order to simplify the representation of calorimetric phenomena in continuum mechanics a hybrid free energy density is introduced. Its canonical independent variables are the isochoric Green strain tensor, the pressure and the temperature. It is related to the Helmholtz free energy density by a Legendre transformation. In combination with the additive split of the stress power into the sum of isochoric and volumetric terms this approach leads to thermomechanical consistent constitutive models for large deformations. The article closes with applications of this approach to finite thermoelasticity, curing adhesives and the glass transition.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In engineering, constitutive theories are usually formulated to represent mechanical material properties under isothermal conditions. In this context, the reader is referred to the articles of Lion (1997), Boyce et al. (2000), Laiarinandrasana et al. (2009), Miehe et al. (2009) or Johlitz et al. (2010) in which the temperature-dependent stress–strain behaviour of elastomers and other polymers under finite deformations is addressed. Since stress- or temperature-induced changes in volume are relatively small under typical loading states and magnitudes, the stress–strain behaviour of a large number of polymers can be assumed as nearly isochoric. Accordingly, under such loadings the effect of the volumetric part of the constitutive model to the stress–strain response is relatively small, for example in the case of tensional loadings of tall specimens. In order to identify the material parameters of constitutive models or to implement them into finite element programs, formulations in which the stress tensor is the dependent mechanical state variable are required. For this reason, the specific Helmholtz free energy is usually taken as fundamental thermodynamic potential in continuum mechanics. It should be mentioned that the isochoric specific heat which is needed for the evaluation of the related differential equation of heat conduction can easily be calculated from the Helmholtz free energy because it is its thermodynamically associated caloric quantity. But caused by their high bulk modulus, the isochoric specific heat cannot be measured for solids. If, for example, the isobaric specific heat has been measured in a standard calorimetric experiment but the isochoric specific heat is needed as input parameter for a finite element program, the difference between them is frequently ignored because in many situations it has minor influence to the simulation results. Following Haupt (2002), in linear thermoelasticity the isochoric and isobaric specific heats c_v and c_p are constant material parameters and are connected as follows:

$$c_p - c_v = \frac{9\theta_0 K \alpha^2}{\rho} \tag{1}$$

The application of (1) is only possible in sufficient small temperature intervals in which c_v and c_p are nearly constant. In the case of polymers, the mass density is about $\rho \approx 10^3 \text{ kg m}^{-3}$, a typical value for the bulk modulus is about $K \approx 3000 \text{ MPa}$, the linear thermal expansion coefficient is of the order of $\alpha \approx 10^{-4} \text{ K}^{-1}$ and $\theta_0 \approx 300 \text{ K}$ is a rough estimate for the reference temperature. Based on these values, $9\theta_0 K \alpha^2 / \rho \approx 81 \text{ J kg}^{-1} \text{ K}^{-1}$ is calculated. Since $c_p - c_v$ depends in a quadratic manner on the expansion coefficient, a larger value of $\alpha \approx 2 \times 10^{-4} \text{ K}^{-1}$ leads to $9\theta_0 K \alpha^2 / \rho \approx 324 \text{ J kg}^{-1} \text{ K}^{-1}$. Assuming $c_p \approx 1500 \text{ J kg}^{-1} \text{ K}^{-1}$ as a typical value

---

* Corresponding author. Tel.: +49 (0) 89 60042494; fax: +49 (0) 89 60042386.
  E-mail address: alexander.lion@unibw.de (A. Lion).

for the isobaric specific heat of polymers, the relative difference $(c_p - c_v)/c_p$ is between 5% and more than 20%. In the case of mechanically incompressible but thermally expandable materials like rubber, the term "isochoric specific heat" makes no sense.

In thermochemistry, on the other hand, the caloric material properties as well as the thermal expansion behaviour are often in the centre of interest (cf. Kamal et al., 1973; Bauer et al., 2000; Gutzow et al., 2007; Garden, 2007a,b; Bailey et al., 2008; Richert, 2011 and the citations therein). In order to represent this type of material behaviour, the specific Gibbs free energy is typically taken as fundamental thermodynamic potential (cf. Gutzow et al., 2007; Lion et al., 2011). The main reason for this choice is the fact that calorimetric and thermal expansion experiments are commonly carried out under prescribed pressure and temperature histories. In many commercial differential scanning calorimetry apparatuses, the pressure is constant and the temperature is a user-definable function of time. It would be quite strange in this situation to take the specific Helmholtz free energy as thermodynamic potential because its associated caloric quantity is the isochoric specific heat. In the case of isotropic materials under free boundary conditions, only changes in volume occur when the pressure and the temperature are varying. Therefore, the isochoric part of a three-dimensional constitutive model (cf. Lion et al., 2010; Lion et al., 2011) has no influence to the caloric response and the thermal expansion behaviour. Consequently, Gutzow et al. (2007) formulated their model only for the volumetric material behaviour, i.e. the Gibbs free energy depends on temperature, pressure and an internal variable which they denoted as order parameter. The application of the Gibbs free energy approach in the field of three-dimensional solid mechanics is promising in the case of linear thermoviscoelasticity (cf. Lion et al., 2010) when the mechanical model is solvable for the stress tensor. But in the case of large deformations or pronounced physical nonlinearities such a formulation would lead to implicit constitutive equations which are no more solvable for the stress tensor.

In a recent essay by Hartmann et al. (2013), the field-assisted sintering of copper and ceramic powder in graphite tools was modelled, simulated and validated. During these processes, the transient temperature variations can reach several hundred degrees. In order to develop a realistic constitutive model for such a process, not only the knowledge about the temperature-dependent mechanical material behaviour is important but also the consideration of the caloric material behaviour. In the relevant temperature range, the experimental data of the isobaric specific heat of graphite exhibits an increase of more than 120%. As it is common practice, the authors developed a constitutive model that is based on the specific Helmholtz free energy such that the empirical function which they fitted to the experimental curve of the specific heat has to be interpreted as isochoric specific heat. This statement becomes clearly when the time derivative of the volume strain in their differential equation of heat conduction is set to zero and can be justified as follows: Since graphite possesses a relative small linear thermal expansion coefficient of $\alpha \approx 4.6 \times 10^{-6}\,\mathrm{K}^{-1}$, a density of $\rho \approx 1850\,\mathrm{kg\,m^{-3}}$ and a bulk modulus of about $K \approx 6000\,\mathrm{MPa}$, the value of $9\theta_0 K\alpha^2/\rho \approx 0.2\,\mathrm{J\,kg^{-1}\,K^{-1}}$ is obtained for the difference $c_p - c_v$ when $\theta_0 \approx 300\,\mathrm{K}$ is assumed. For this reason, it is not required to distinguish between the isochoric and the isobaric specific heat in the case of graphite at least under small temperature changes. Since the terms isochoric and isobaric are precisely defined, caution is necessary.

These considerations have shown that a temperature- and pressure-dependent free energy of the Gibbs type is advantageous when isobaric caloric or volumetric thermal expansion data have to be constitutively modelled. If mechanical stress–strain data has to be modelled or a finite element implementation has to be realised, it is more convenient to develop a model which is based on the temperature- and deformation-dependent Helmholtz free energy. In order to separate volumetric effects from changes in shape it is useful to split the deformation gradient into the corresponding contributions. For these reasons, a hybrid free energy density is proposed which combines all these aspects. In Section 2 of this paper, the fundamentals and the general thermomechanical framework are provided. In Section 3, it is shown how caloric quantities like the enthalpy rate or the isobaric specific heat can be taken into account in a stringent manner. Section 4 discusses different applications of the theory and Section 5 closes with a discussion.

2. Thermomechanical approach

In order to represent thermomechanical material properties in nonlinear continuum mechanics the space- and time-dependent deformation gradient $\mathbf{F}$ is a fundamental geometrical quantity (cf. Haupt, 2002). Its determinant $J = \det(\mathbf{F})$ describes the ratio of the volume elements between the reference and the current configuration. As proposed by Flory (1961), the tensor $\mathbf{F}$ can be multiplicatively decomposed into pure volumetric and isochoric contributions:

$$\mathbf{F} = \overline{\mathbf{F}}\hat{\mathbf{F}} \tag{2}$$

$$\overline{\mathbf{F}} = J^{1/3}\mathbf{1} \tag{3}$$

$$\hat{\mathbf{F}} = J^{-1/3}\mathbf{F} \tag{4}$$

The isochoric part $\hat{\mathbf{F}}$ is not influenced by changes in volume and the volumetric part $\overline{\mathbf{F}}$ does not depend on changes in shape. Based on the tensors $\mathbf{F}$ and $\hat{\mathbf{F}}$, two different Cauchy–Green tensors $\mathbf{C} = \mathbf{F}^T\mathbf{F}$ and $\hat{\mathbf{C}} = \hat{\mathbf{F}}^T\hat{\mathbf{F}}$ which are calculated with the total deformation gradient and its isochoric part are introduced. This motivates the following definitions of two Green strain tensors and of the volume strain:

$$\mathbf{E} = \frac{1}{2}(\mathbf{C} - \mathbf{1}) \tag{5}$$

$$\hat{\mathbf{E}} = \frac{1}{2}(\hat{\mathbf{C}} - \mathbf{1}) \tag{6}$$

$$\varepsilon_{\mathrm{vol}} = J - 1 \tag{7}$$

Considering these expressions, the total Green strain tensor $\mathbf{E}$ can be expressed as follows:

$$\mathbf{E} = \frac{1}{2}(J^{2/3}\hat{\mathbf{C}} - \mathbf{1}) = J^{2/3}\hat{\mathbf{E}} + \frac{1}{2}(J^{2/3} - 1)\mathbf{1} \tag{8}$$

Since the isochoric Cauchy Green tensor $\hat{\mathbf{C}}$ is unimodular, the constraint $\det(\hat{\mathbf{C}}) = 1$ holds for arbitrary deformation histories. Differentiating this relation with respect to time, the following orthogonality relation can be derived:

$$\frac{\mathrm{d}}{\mathrm{d}t}\det\left(\hat{\mathbf{C}}(t)\right) = 0 \quad \Rightarrow \quad \hat{\mathbf{C}}^{-1} \cdot \dot{\hat{\mathbf{C}}} = 0 \tag{9}$$

The dot between two second order tensors is the scalar product, $\mathbf{A} \cdot \mathbf{B} = \mathrm{tr}\left(\mathbf{A}\mathbf{B}^T\right) = \sum_{i,k=1}^{3} A_{ik}B_{ik}$, and $\mathrm{tr}(\mathbf{A}) = A_{11} + A_{22} + A_{33}$ is the trace of the second order tensor $\mathbf{A}$. In order to separate volumetric and isochoric effects also with regard to the stress, the Cauchy stress tensor $\mathbf{T}$ is represented as the sum of a spherical and a deviatoric part:

$$\mathbf{T} = -p\mathbf{1} + \mathbf{T}^D \tag{10}$$

$$p = -\frac{1}{3}\mathrm{tr}(\mathbf{T}) \tag{11}$$

$$\mathbf{T}^{\mathrm{D}} = \mathbf{T} - \frac{1}{3}\operatorname{tr}(\mathbf{T})\mathbf{1} \tag{12}$$

Motivated by these decompositions, two additional stress tensors are defined. The first tensor is the well-known second Piola–Kirchhoff stress:

$$\widetilde{\mathbf{T}} = J\mathbf{F}^{-1}\mathbf{T}\mathbf{F}^{\mathrm{T}-1} \tag{13}$$

The second tensor is of the same type but calculated with the deviator (12) of the Cauchy stress and the isochoric part of the deformation gradient:

$$\hat{\widetilde{\mathbf{T}}} = J\hat{\mathbf{F}}^{-1}\mathbf{T}^{\mathrm{D}}\hat{\mathbf{F}}^{\mathrm{T}-1} \tag{14}$$

A short calculation leads to:

$$\widetilde{\mathbf{T}} = -pJ^{1/3}\hat{\mathbf{C}}^{-1} + J^{-2/3}\hat{\widetilde{\mathbf{T}}} \tag{15}$$

On the basis of (8) in combination with (13) and (15) the stress power per unit volume of the reference configuration can be expressed as follows:

$$\widetilde{\mathbf{T}} \cdot \dot{\mathbf{E}} = \left(-pJ^{1/3}\hat{\mathbf{C}}^{-1} + J^{-2/3}\hat{\widetilde{\mathbf{T}}} \right) \cdot \frac{\mathrm{d}}{\mathrm{d}t}\left(J^{2/3}\hat{\mathbf{E}} + \frac{1}{2}(J^{2/3} - 1)\mathbf{1} \right) \tag{16}$$

Differentiating the Green strain tensor on the right-hand side of (16) under consideration of the product rule, an intermediate result is obtained:

$$\widetilde{\mathbf{T}} \cdot \dot{\mathbf{E}} = \left(-pJ^{1/3}\hat{\mathbf{C}}^{-1} + J^{-2/3}\hat{\widetilde{\mathbf{T}}} \right) \cdot \left(\frac{2}{3}\frac{\dot{J}}{J^{1/3}}\hat{\mathbf{E}} + \frac{1}{3}\frac{\dot{J}}{J^{1/3}}\mathbf{1} + J^{2/3}\dot{\hat{\mathbf{E}}} \right)$$

Expanding this expression and rearranging terms leads to:

$$\widetilde{\mathbf{T}} \cdot \dot{\mathbf{E}} = -\frac{p\dot{J}}{3}\hat{\mathbf{C}}^{-1} \cdot (\mathbf{1} + 2\hat{\mathbf{E}}) - pJ\hat{\mathbf{C}}^{-1} \cdot \dot{\hat{\mathbf{E}}} + \frac{1}{3}\frac{\dot{J}}{J}\hat{\widetilde{\mathbf{T}}} \cdot (\mathbf{1} + 2\hat{\mathbf{E}}) + \hat{\widetilde{\mathbf{T}}} \cdot \dot{\hat{\mathbf{E}}} \tag{17}$$

Considering the relations

$$\hat{\mathbf{C}}^{-1} \cdot (\mathbf{1} + 2\hat{\mathbf{E}}) = \hat{\mathbf{C}}^{-1} \cdot \hat{\mathbf{C}} = \operatorname{tr}(\hat{\mathbf{C}}^{-1}\hat{\mathbf{C}}) = 3$$

$$\hat{\mathbf{C}}^{-1} \cdot \dot{\hat{\mathbf{E}}} = 1/2\hat{\mathbf{C}}^{-1} \cdot \dot{\hat{\mathbf{C}}} = 0$$

$$\hat{\widetilde{\mathbf{T}}} \cdot (\mathbf{1} + 2\hat{\mathbf{E}}) = \hat{\widetilde{\mathbf{T}}} \cdot \hat{\mathbf{C}} = J\operatorname{tr}(\mathbf{T}^{\mathrm{D}}) = 0$$

the right-hand side of (17) can be simplified. The corresponding result shows that the total stress power is the sum of a pure volumetric and a pure isochoric contribution:

$$\widetilde{\mathbf{T}} \cdot \dot{\mathbf{E}} = -p\dot{\varepsilon}_{\mathrm{vol}} + \hat{\widetilde{\mathbf{T}}} \cdot \dot{\hat{\mathbf{E}}} \tag{18}$$

If the strain-dependent Helmholtz free energy density is used as thermodynamic potential, the Green strain tensor (5) or, alternatively, both the isochoric Green strain tensor (6) and the volume strain (7) can be used as independent mechanical state variables. If, on the other hand, the stress-dependent Gibbs free energy density is used as thermodynamic potential, the Cauchy stress tensor (10) or, alternatively, the hydrostatic pressure (11) in combination with the deviatoric stress tensor (12) are the mechanical state variables. As motivated in the last section, it makes sense to introduce a hybrid free energy density which should depend on the isochoric Green strain tensor in combination with the hydrostatic pressure as mechanical state variables.

In order to define the hybrid free energy function φ the volume strain $\varepsilon_{\mathrm{vol}}$ is replaced by the hydrostatic pressure p using a Legendre transformation. It depends on the Helmholtz free energy per unit mass ψ, the volume strain (7), the pressure (11) and the mass density ρ_{R} of the reference configuration:

$$\varphi = \psi + \frac{1}{\rho_{\mathrm{R}}}p\varepsilon_{\mathrm{vol}} \tag{19}$$

For the purpose of formulating thermomechanical consistent material models on the basis of the hybrid free energy function φ, (18) and (19) have to be inserted into the Clausius–Duhem inequality (cf. Haupt, 2002). It reads as follows and states that the rate of dissipation has to be nonnegative:

$$-\rho_{\mathrm{R}}\dot{\psi} + \widetilde{\mathbf{T}} \cdot \dot{\mathbf{E}} - \rho_{\mathrm{R}}s\dot{\theta} - \frac{\vec{q}_{\mathrm{R}} \cdot \vec{g}_{\mathrm{R}}}{\theta} \geqslant 0 \tag{20}$$

The variable s is the entropy per unit mass, $\vec{q}_{\mathrm{R}}$ the heat flux vector and $\vec{g}_{\mathrm{R}}$ the temperature gradient. The time derivatives in (20) inspire that the canonical independent variables of the specific Helmholtz free energy are the Green strain tensor and the absolute temperature, i.e. $\psi = \psi(\mathbf{E}, \theta, \ldots)$. The dots indicate optional dependences on internal state variables. Inserting (18) and (19) into (20) the following expression is obtained:

$$-\rho_{\mathrm{R}}\dot{\varphi} + \hat{\widetilde{\mathbf{T}}} \cdot \dot{\hat{\mathbf{E}}} + \varepsilon_{\mathrm{vol}}\dot{p} - \rho_{\mathrm{R}}s\dot{\theta} - \frac{\vec{q}_{\mathrm{R}} \cdot \vec{g}_{\mathrm{R}}}{\theta} \geqslant 0 \tag{21}$$

The time derivatives in (21) motivate that the isochoric Green strain tensor, the pressure and the temperature define the canonical variables of φ:

$$\varphi = \varphi(\hat{\mathbf{E}}, p, \theta, \ldots) \tag{22}$$

The dependence of (22) on $\hat{\mathbf{E}}$ and p establishes the denotation of φ as hybrid free energy density. In order to model inelastic material behaviour, additional arguments are introduced:

$$\varphi = \varphi(p, \hat{\mathbf{E}}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_{\mathrm{n}}, q_1, \ldots, q_{\mathrm{m}}) \tag{23}$$

The internal state variables $\mathbf{Q}_{\mathrm{k}}$ are tensors of the second order, for example overstresses or inelastic strains. The variables q_{k} are scalar quantities, for example order parameters or variables describing the progress of chemical reactions.

Calculating the time rate of (23) and inserting the outcome into (21) the following expression is derived:

$$\left(\hat{\widetilde{\mathbf{T}}} - \rho_{\mathrm{R}}\frac{\partial\varphi}{\partial\hat{\mathbf{E}}} \right) \cdot \dot{\hat{\mathbf{E}}} + \left(\varepsilon_{\mathrm{vol}} - \rho_{\mathrm{R}}\frac{\partial\varphi}{\partial p} \right)\dot{p} - \rho_{\mathrm{R}}\left(s + \frac{\partial\varphi}{\partial\theta} \right)\dot{\theta}$$
$$- \rho_{\mathrm{R}}\left(\frac{\partial\varphi}{\partial\mathbf{Q}_{\mathrm{k}}} \cdot \dot{\mathbf{Q}}_{\mathrm{k}} + \frac{\partial\varphi}{\partial q_{\mathrm{k}}}\dot{q}_{\mathrm{k}} \right) - \frac{\vec{q}_{\mathrm{R}} \cdot \vec{g}_{\mathrm{R}}}{\theta}$$
$$\geqslant 0 \tag{24}$$

In order to satisfy this inequality for arbitrary values of the time derivatives of $\hat{\mathbf{E}}$, p and θ, three potential relations and a residual inequality are obtained:

$$\hat{\widetilde{\mathbf{T}}} = \rho_{\mathrm{R}}\frac{\partial\varphi}{\partial\hat{\mathbf{E}}} + \Phi\hat{\mathbf{C}}^{-1}, \quad \varepsilon_{\mathrm{vol}} = \rho_{\mathrm{R}}\frac{\partial\varphi}{\partial p}, \quad s = -\frac{\partial\varphi}{\partial\theta} \tag{25}$$

$$-\rho_{\mathrm{R}}\left(\frac{\partial\varphi}{\partial\mathbf{Q}_{\mathrm{k}}} \cdot \dot{\mathbf{Q}}_{\mathrm{k}} + \frac{\partial\varphi}{\partial q_{\mathrm{k}}}\dot{q}_{\mathrm{k}} \right) - \frac{\vec{q}_{\mathrm{R}} \cdot \vec{g}_{\mathrm{R}}}{\theta} \geqslant 0 \tag{26}$$

The additional term in the potential relation for the stress tensor should be commented: If the five independent components of the isochoric strain rate tensor $\hat{\mathbf{E}}$ are varied arbitrarily, it cannot be concluded that $\hat{\widetilde{\mathbf{T}}} - \rho_{\mathrm{R}}\partial\varphi/\partial\hat{\mathbf{E}} = \mathbf{0}$ when the non-negativity of the rate of dissipation is required. Owing to $\hat{\mathbf{E}} = 1/2\hat{\mathbf{C}}$ and the orthogonality relation $\hat{\mathbf{C}}^{-1} \cdot \dot{\hat{\mathbf{C}}} = 0$ (see (9) for details) the logical consequence is $\hat{\widetilde{\mathbf{T}}} - \rho_{\mathrm{R}}\partial\varphi/\partial\hat{\mathbf{E}} = \Phi\hat{\mathbf{C}}^{-1}$ with an arbitrary scalar Φ. It can be easily determined when the deviator of the Cauchy stress is calculated via (14) and (25):

$$\mathbf{T}^{\mathrm{D}} = \frac{1}{J}\hat{\mathbf{F}}\hat{\widetilde{\mathbf{T}}}\hat{\mathbf{F}}^{\mathrm{T}} = \frac{1}{J}\left(\rho_{\mathrm{R}}\hat{\mathbf{F}}\frac{\partial\varphi}{\partial\hat{\mathbf{E}}}\hat{\mathbf{F}}^{\mathrm{T}} + \Phi\mathbf{1} \right) \tag{27}$$

The requirement that the right-hand side of (27) has to be a deviator leads to the solution

$$\Phi = -\frac{1}{3}\rho_R\left(\hat{\mathbf{F}}\frac{\partial\varphi}{\partial\hat{\mathbf{E}}}\hat{\mathbf{F}}^T\right)\cdot\mathbf{1} = -\frac{1}{3}\rho_R\frac{\partial\varphi}{\partial\hat{\mathbf{E}}}\cdot\hat{\mathbf{C}} \tag{28}$$

and finally to the following relation for the isochoric second Piola Kirchhoff stress:

$$\hat{\tilde{\mathbf{T}}} = \rho_R\left(\frac{\partial\varphi}{\partial\hat{\mathbf{E}}} - \frac{1}{3}\left(\frac{\partial\varphi}{\partial\hat{\mathbf{E}}}\cdot\hat{\mathbf{C}}\right)\hat{\mathbf{C}}^{-1}\right) \tag{29}$$

The model structure which is based on the hybrid free energy density defined by (19) leads to potential relations for the isochoric part of the second Piola Kirchhoff stress tensor, the volume strain and the specific entropy. In order to calculate the total second Piola Kirchhoff stress tensor $\tilde{\mathbf{T}}$ via (15) the potential relation for the volume strain (25) has to be inverted in the following sense: $p = f(\varepsilon_{vol}, \theta, \ldots)$. The residual inequality (26) has to be satisfied by the evolution equations for the internal state variables and the constitutive model for the heat flux.

3. Caloric behaviour of isotropic materials under constant pressure

In order to simulate the caloric behaviour of a material under arbitrary temperature histories and spherical states of stress, the local balance equation of energy must be taken into account. The representation (18) of the stress power simplifies the consideration of such conditions and the assumption $\mathbf{T} = -p\mathbf{1}$ or $\mathbf{T}^D = \mathbf{0}$ in combination with (14) leads to the following relation:

$$\rho_R\dot{e} = -p\dot{J} - \text{div}(\vec{q}_R) + \rho_R r \tag{30}$$

The scalar e is the internal energy per unit mass and r is the volume-distributed heat supply. In order to structure the theory, isotropic material behaviour is assumed and the hybrid free energy function (23) is defined as the sum of a volumetric and an isochoric part:

$$\varphi = \varphi_{vol}(p, \hat{\mathbf{E}}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_n, q_1, \ldots, q_m)$$
$$+ \varphi_{iso}(p, \hat{\mathbf{E}}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_n, q_1, \ldots, q_m) \tag{31}$$

Since the material is isotropic and the stress state is purely spherical no changes in shape take place when the temperature or the pressure are varied, i.e. $\hat{\mathbf{E}} \equiv \mathbf{0}$ holds for all times. For physical reasons, the isochoric part of (31) vanishes in this situation:

$$\varphi_{iso}(p, \mathbf{0}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_n, q_1, \ldots, q_m) = 0 \tag{32}$$

If the specific internal energy is also represented as $e = e_{vol} + e_{iso}$ then $e_{iso} = 0$ holds as well. Considering this in combination with the assumption $r = 0$, the following relations are found:

$$\rho_R\dot{e}_{vol} = -p\dot{J} - \text{div}(\vec{q}_R) \tag{33}$$

$$\varphi = \varphi_{vol} \tag{34}$$

In order to express the volumetric part of the internal energy density e_{vol} by that of the hybrid free energy φ_{vol} the following Legendre transformation is applied:

$$e_{vol} = \psi_{vol} + \theta s_{vol} \tag{35}$$

Combining (25) with (31) and (32) the volumetric part of the entropy per unit mass reads as $s_{vol} = -\partial\varphi_{vol}/\partial\theta$. If (7) and (19) are taken into account, e_{vol} can be written as follows:

$$e_{vol} = \left(\varphi_{vol} - \frac{1}{\rho_R}p(J-1)\right) - \theta\frac{\partial\varphi_{vol}}{\partial\theta} \tag{36}$$

Differentiating (36) with respect to the time,

$$\dot{e}_{vol} = \frac{\partial\varphi_{vol}}{\partial\theta}\dot{\theta} + \frac{\partial\varphi_{vol}}{\partial p}\dot{p} + \frac{\partial\varphi_{vol}}{\partial\hat{\mathbf{E}}}\cdot\dot{\hat{\mathbf{E}}} + \frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k}\cdot\dot{\mathbf{Q}}_k + \frac{\partial\varphi_{vol}}{\partial q_k}\dot{q}_k$$
$$-\frac{1}{\rho_R}\dot{p}(J-1) - \frac{1}{\rho_R}p\dot{J} - \dot{\theta}\frac{\partial\varphi_{vol}}{\partial\theta}$$
$$-\theta\left(\frac{\partial^2\varphi_{vol}}{\partial\theta^2}\dot{\theta} + \frac{\partial^2\varphi_{vol}}{\partial p\partial\theta}\dot{p} + \frac{\partial^2\varphi_{vol}}{\partial\hat{\mathbf{E}}\partial\theta}\cdot\dot{\hat{\mathbf{E}}} + \frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\cdot\dot{\mathbf{Q}}_k + \frac{\partial^2\varphi_{vol}}{\partial q_k\partial\theta}\dot{q}_k\right)$$

assuming $\dot{p} = 0$, considering $\dot{\hat{\mathbf{E}}} = \mathbf{0}$ and rearranging terms leads to

$$\dot{e}_{vol} = \left(\frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\right)\cdot\dot{\mathbf{Q}}_k + \left(\frac{\partial\varphi_{vol}}{\partial q_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial q_k\partial\theta}\right)\dot{q}_k$$
$$-\frac{1}{\rho_R}p\dot{J} - \theta\frac{\partial^2\varphi_{vol}}{\partial\theta^2}\dot{\theta} \tag{37}$$

Inserting (37) into (33), the following expression is obtained:

$$-\frac{1}{\rho_R}\text{div}(\vec{q}_R) = \left(\frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\right)\cdot\dot{\mathbf{Q}}_k$$
$$+ \left(\frac{\partial\varphi_{vol}}{\partial q_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial q_k\partial\theta}\right)\dot{q}_k - \theta\frac{\partial^2\varphi_{vol}}{\partial\theta^2}\dot{\theta} \tag{38}$$

In order to calculate the total heat power $P_{DSC}(t)$ which is transferred to or emitted from a test specimen with density ρ_R, mass m, volume V and surface area A, (38) is integrated over its volume. In Fig. 1, such a situation is sketched in combination with the normal vector $\vec{N}_R$ and the heat flux vector $\vec{q}_R$.

Applying the Gauss theorem, the left-hand side of (38) can be rewritten as follows:

$$-\frac{1}{\rho_R}\int_V\text{div}(\vec{q}_R)dV = -\frac{1}{\rho_R}\int_V\vec{q}_R\cdot\vec{N}_R dA = \frac{P_{DSC}(t)}{\rho_R} \tag{39}$$

The minus sign is not adapted to the right-hand side of (39) because the heat power $P_{DSC}(t)$ should be positive when heat is transferred to the specimen. In this case, the scalar product $\vec{q}_R\cdot\vec{N}_R$ between the heat flux and the normal vector is negative. Assuming homogeneous conditions, the integration of the right-hand side of (38) over the volume leads to:

$$\int_V\left(\left(\frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\right)\cdot\dot{\mathbf{Q}}_k + \cdots\right)dV$$
$$= V\left(\left(\frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\right)\cdot\dot{\mathbf{Q}}_k + \cdots\right) \tag{40}$$

In view of $m = \rho_R V$ the final result of the volume integration of (38) reads as follows:

$$\frac{P_{DSC}(t)}{m} = \left(\frac{\partial\varphi_{vol}}{\partial\mathbf{Q}_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial\mathbf{Q}_k\partial\theta}\right)\cdot\dot{\mathbf{Q}}_k + \left(\frac{\partial\varphi_{vol}}{\partial q_k} - \theta\frac{\partial^2\varphi_{vol}}{\partial q_k\partial\theta}\right)\dot{q}_k - \theta\frac{\partial^2\varphi_{vol}}{\partial\theta^2}\dot{\theta} \tag{41}$$
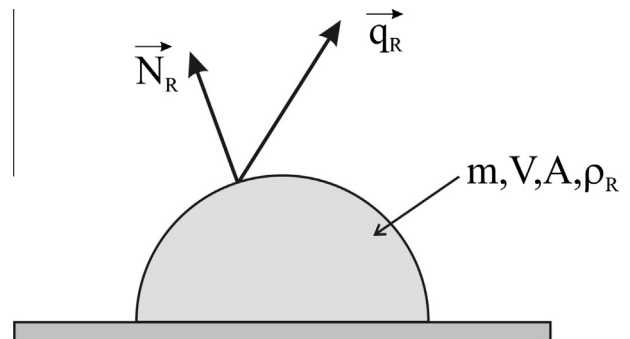

Fig. 1. Heat flux and normal vector of a test specimen in a calorimeter.

The right-hand side of (41) can be formulated more clearly when the volumetric part of the specific enthalpy h_{vol} is introduced. To this end, the Legendre transformation

$$h_{\mathrm{vol}} = e_{\mathrm{vol}} + \frac{1}{\rho_{\mathrm{R}}} p(J-1) \tag{42}$$

is applied and (36) is taken into account:

$$h_{\mathrm{vol}} = \varphi_{\mathrm{vol}} - \theta \frac{\partial \varphi_{\mathrm{vol}}}{\partial \theta} \tag{43}$$

Differentiating (43) with respect to time under consideration of (31), (32), $\dot{p} = 0$ and $\dot{\mathbf{E}} = \mathbf{0}$ leads to:

$$\dot{h}_{\mathrm{vol}}\Big|_{p=\mathrm{const}} = \left(\frac{\partial \varphi_{\mathrm{vol}}}{\partial \mathbf{Q}_{\mathrm{k}}} - \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \mathbf{Q}_{\mathrm{k}} \partial \theta} \right) \cdot \dot{\mathbf{Q}}_{\mathrm{k}} + \left(\frac{\partial \varphi_{\mathrm{vol}}}{\partial q_{\mathrm{k}}} - \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial q_{\mathrm{k}} \partial \theta} \right) \dot{q}_{\mathrm{k}}$$
$$- \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \theta^2} \dot{\theta} \tag{44}$$

Comparing (44) with (41) a well-known result is obtained: the heat power per unit mass is equal to the material time-rate of the specific enthalpy under constant pressure (cf. Lion et al., 2011; Lion et al., 2010; Lion and Yagimli, 2009):

$$\frac{P_{\mathrm{DSC}}(t)}{m} = \frac{\mathrm{d}}{\mathrm{d}t} h_{\mathrm{vol}}(p, \mathbf{0}, \theta, \mathbf{Q}_1, \dots, \mathbf{Q}_n, q_1, \dots, q_m)\Big|_{p=\mathrm{const}} \tag{45}$$

The experimental technique of differential scanning calorimetry (acronym: DSC) can measure the total heat power $P_{\mathrm{DSC}}(t)$ which is transferred to or emitted from a test specimen under prescribed temperature histories at constant pressure. In (41), (45), the internal variables express the influence of process-dependent changes in the microstructure, in the molecular configuration or the in chemical structure of the material to the heat exchange with the environment under isobaric conditions.

In the elementary theory of thermodynamics, the isobaric specific heat c_{p} per unit mass is defined as the amount of heat ΔQ which has to be supplied to the quantity $m = 1$ kg of a given material under constant pressure in order to raise its temperature by $\Delta \theta = 1$ K:

$$c_{\mathrm{p}} = \frac{\Delta Q}{m \Delta \theta}\Big|_{p=\mathrm{const}} \tag{46}$$

Considering the definition (46) the following expression for the isobaric specific heat is used in this article (cf. Lion et al., 2010; Lion et al., 2011):

$$c_{\mathrm{p}} = \frac{P_{\mathrm{DSC}}}{\dot{\theta} m} = -\theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \theta^2} + \frac{1}{\dot{\theta}} \left(\frac{\partial \varphi_{\mathrm{vol}}}{\partial \mathbf{Q}_{\mathrm{k}}} - \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \mathbf{Q}_{\mathrm{k}} \partial \theta} \right) \cdot \dot{\mathbf{Q}}_{\mathrm{k}}$$
$$+ \frac{1}{\dot{\theta}} \left(\frac{\partial \varphi_{\mathrm{vol}}}{\partial q_{\mathrm{k}}} - \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial q_{\mathrm{k}} \partial \theta} \right) \dot{q}_{\mathrm{k}} = \frac{\dot{h}_{\mathrm{vol}}}{\dot{\theta}}\Big|_{p=\mathrm{const}} \tag{47}$$

In (47), also time-dependent changes in the internal variables contribute to c_{p}. A definition of this form has to be applied, for example, when the complex frequency-dependent specific heat has to be calculated (cf. Lion and Yagimli, 2009; Lion et al., 2010) or when the thermoreversible glass transition is constitutively modelled (cf. Lion et al., 2012). It should be noted that the application of the term "specific heat" and its interpretation become questionable when exo- or endothermic chemical reactions take place within the material. In such situations, it makes more sense, to consider the heat power per unit mass $P_{\mathrm{DSC}}(t)/m$ directly which equals the temporal rate of change in the specific enthalpy as specified in (45). In traditional textbooks of continuum mechanics (e.g. Haupt, 2002), only the first term in (47) which contains the second derivative of the thermodynamic potential with respect to the absolute temperature is defined as specific heat. This definition

coincides with (47) only when the internal state of the material does not change during the caloric experiment, i.e. the time rates of all internal variables have to be zero. Accordingly, the expression

$$c_{\mathrm{p}} = -\theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \theta^2} \tag{48}$$

is only applicable in the case of perfect thermoelastic material behaviour without any history effects or structural changes.

4. Examples

4.1. Finite thermoelasticity

Now, the developed theory is applied in the context of finite thermoelasticity. To this end, the volumetric part of the hybrid free energy is assumed to be independent on the isochoric strain tensor and the isochoric part of φ is postulated to be independent on the pressure:

$$\varphi = \varphi_{\mathrm{vol}}(p, \theta) + \varphi_{\mathrm{iso}}(\hat{\mathbf{E}}, \theta) \tag{49}$$

In order to determine the function $\varphi_{\mathrm{vol}}(p, \theta)$, the temperature dependence of the specific heat was measured under constant pressure. In this situation, only changes in volume take place such that $\hat{\mathbf{E}} = \mathbf{0}$ and, as a consequence, $\varphi_{\mathrm{iso}} = 0$ holds. In Fig. 2, the isobaric specific heat per unit mass of a special type of carbon black-filled rubber is plotted as a function of the absolute temperature. The test was carried out with a differential scanning calorimeter produced by the NETZSCH Company in Selb, Germany. The temperature rate was 10 K/min. Since the glass transition temperature of this elastomer is at about 210 K the test was driven in the entropy elastic range in which the specific heat exhibits no rate dependence. In a first approximation, the isobaric specific heat can be represented by a linear function of the temperature:

$$c_{\mathrm{p}} = c_{\mathrm{p}0} + \beta(\theta - \theta_0) \tag{50}$$

$$c_{\mathrm{p}0} = 1620 \frac{\mathrm{J}}{\mathrm{kg\,K}}, \quad \beta = 3.6 \frac{\mathrm{J}}{\mathrm{kg^2\,K}}, \quad \theta_0 = 300\,\mathrm{K}$$

The reference temperature θ_0 was prescribed and the two other parameters were identified by standard methods. Fig. 2 shows that the representation of the experimental curve is sufficient. The maximum error is about 7%. In order to calculate the volumetric part of the hybrid free energy, (50) is inserted into (48):

$$\frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \theta^2} = -\frac{c_{\mathrm{p}0} - \beta \theta_0}{\theta} - \beta \tag{51}$$
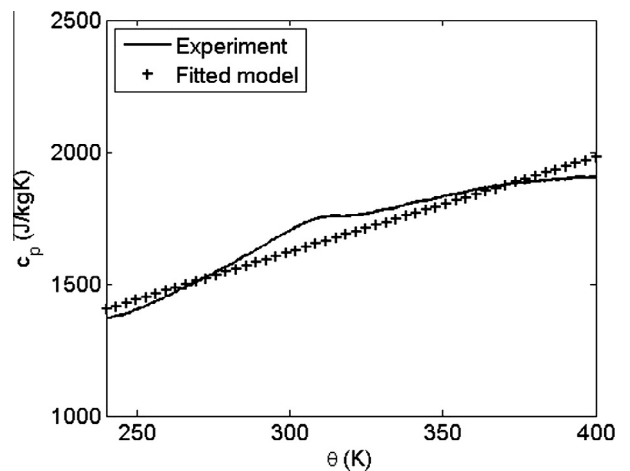
Fig. 2. Isobaric specific heat of a carbon black-filled elastomer.

The double integration of (51) with regard to the temperature θ leads to

$$\varphi_{\text{vol}} = -(c_{p0} - \beta\theta_0)(\theta \ln\theta - \theta) - \frac{\beta}{2}\theta^2 + C(p)\theta + D(p) \tag{52}$$

This expression contains two pressure-dependent integration constants $C(p)$ and $D(p)$. Since φ_{iso} is independent on p as assumed in (49), they can be determined when the potential relation for the volume strain (25) is applied:

$$\varepsilon_{\text{vol}}(p, \theta) = \rho_R \frac{\partial}{\partial p}(\varphi_{\text{vol}} + \varphi_{\text{iso}}) = \rho_R \frac{\partial\varphi_{\text{vol}}}{\partial p}$$
$$= \rho_R(C'(p)\theta + D'(p)) \tag{53}$$

Since the mechanical behaviour of elastomers is nearly incompressible in the entropy elastic regime and the thermal expansion effects are relatively small, the volume strain (53) can be assumed to depend linearly on both the pressure and the temperature. This idea motivates the following structure in which α, ζ and η are additional material constants:

$$\rho_R C'(p) = \alpha, \quad \rho_R D'(p) = \zeta p + \eta \tag{54}$$

If the pressure is zero, (53) and (54) lead to $\varepsilon_{\text{vol}}(0, \theta) = \alpha\theta + \eta$. The definition of the zero-point $\varepsilon_{\text{vol}}(0, \theta_0) = 0$ leads to $\eta = -\alpha\theta_0$ and finally to $\varepsilon_{\text{vol}}(0, \theta) = \alpha(\theta - \theta_0)$ such that α is the volumetric thermal expansion coefficient. If, on the other hand, $\theta = \theta_0$ is assumed, (53) and (54) lead to $\varepsilon_{\text{vol}}(p, \theta_0) = \zeta p$ such that $\zeta = -1/\kappa$ is the negative reciprocal bulk modulus. Taking this study into account, the following relations are obtained for the volume strain and the volumetric part of the hybrid free energy density:

$$\varepsilon_{\text{vol}} = \alpha(\theta - \theta_0) - \frac{1}{\kappa}p \tag{55}$$

$$\varphi_{\text{vol}} = -(c_{p0} - \beta\theta_0)(\theta \ln\theta - \theta) - \frac{\beta}{2}\theta^2 + C_0\theta + D_0 + \frac{\alpha}{\rho_R}(\theta - \theta_0)p - \frac{1}{2\rho_R\kappa}p^2 \tag{56}$$

C_0 and D_0 are integration constants. If the isochoric part $\varphi_{\text{iso}}(\hat{\mathbf{E}}, \theta)$ of the hybrid free energy is also given, the second Piola–Kirchhoff stress tensor can be calculated when the definition $\mathbf{C} = J^{2/3}\hat{\mathbf{C}}$ as well as 15, 29, 49, and (55) are considered:

$$\widetilde{\mathbf{T}} = \kappa J(J - 1 - \alpha(\theta - \theta_0))\mathbf{C}^{-1}$$
$$+ \rho_R J^{-2/3}\left(\frac{\partial\varphi_{\text{iso}}}{\partial\hat{\mathbf{E}}} - \frac{1}{3}\left(\frac{\partial\varphi_{\text{iso}}}{\partial\hat{\mathbf{E}}} \cdot \mathbf{C}\right)\mathbf{C}^{-1}\right) \tag{57}$$

The calculation of the second Piola–Kirchhoff stress in closed form requires to transform the $\varepsilon_{\text{vol}} = F(p, \theta)$ relation to $p = f(\varepsilon_{\text{vol}}, \theta)$. In the case of a linear equation such as (55) this calculation is easy.

In order to demonstrate that (57) represents reasonable material behaviour, the thermoelastic inversion effect (cf. Treloar, 1975; Ogden, 1992) is simulated. To this end, the total length or the stretch $\lambda > 1$ of a test specimen under tension is kept constant, the temperature is varied and the temperature-induced changes in the stress are calculated. For the function $\varphi_{\text{iso}}(\hat{\mathbf{E}}, \theta)$ an entropy elastic Neo-Hookean model with the material constant μ is assumed:

$$\rho_R \varphi_{\text{iso}} = \mu \frac{\theta}{\theta_0}(\hat{\mathbf{C}} \cdot \mathbf{1} - 3) \tag{58}$$

Considering $\partial/\partial\hat{\mathbf{E}} = 2\partial/\partial\hat{\mathbf{C}}$ in combination with (13) and (57) as well as the definition of the left Cauchy–Green tensor $\mathbf{B} = \mathbf{FF}^T$ the Cauchy stress tensor reads as follows:

$$\mathbf{T} = \kappa(J - 1 - \alpha(\theta - \theta_0))\mathbf{1} + 2J^{-5/3}\mu\frac{\theta}{\theta_0}\left(\mathbf{B} - \frac{1}{3}(\mathbf{1} \cdot \mathbf{B})\mathbf{1}\right) \tag{59}$$

Evaluating this relation for uniaxial tension,

$$\mathbf{F} = \lambda\vec{e}_1 \otimes \vec{e}_1 + \lambda_{\text{lat}}(\vec{e}_2 \otimes \vec{e}_2 + \vec{e}_3 \otimes \vec{e}_3), \quad \mathbf{T} = \sigma\vec{e}_1 \otimes \vec{e}_1 \tag{60}$$

and calculating $J = \lambda\lambda_{\text{lat}}^2$, two equations to compute the lateral stretch λ_{lat} and the stress σ are obtained:

$$\sigma = \kappa(\lambda\lambda_{\text{lat}}^2 - 1 - \alpha(\theta - \theta_0)) + \frac{4}{3}(\lambda\lambda_{\text{lat}}^2)^{-5/3}\mu\frac{\theta}{\theta_0}(\lambda^2 - \lambda_{\text{lat}}^2) \tag{61}$$

$$0 = \kappa(\lambda\lambda_{\text{lat}}^2 - 1 - \alpha(\theta - \theta_0)) - \frac{2}{3}(\lambda\lambda_{\text{lat}}^2)^{-5/3}\mu\frac{\theta}{\theta_0}(\lambda^2 - \lambda_{\text{lat}}^2) \tag{62}$$

Rearranging the terms and considering the definition of the first Piola–Kirchhoff stress tensor $\mathbf{T}_R = J\mathbf{TF}^{T-1} = \sigma_R\vec{e}_1 \otimes \vec{e}_1$ with $\sigma_R = \lambda_{\text{lat}}^2\sigma$, the following result is found:

$$\sigma_R = \lambda_{\text{lat}}^2\left(2\mu\frac{\theta}{\theta_0}(\lambda\lambda_{\text{lat}}^2)^{-5/3}(\lambda^2 - \lambda_{\text{lat}}^2)\right) \tag{63}$$

$$\lambda_{\text{lat}}^2 = \frac{1}{\lambda}\left(1 + \frac{2}{3}\frac{\mu}{\kappa}\frac{\theta}{\theta_0}\frac{\lambda^2 - \lambda_{\text{lat}}^2}{(\lambda\lambda_{\text{lat}}^2)^{5/3}} + \alpha(\theta - \theta_0)\right) \tag{64}$$

In order to compute the engineering stress σ_R for given values of stretch λ and temperature θ, (64) has to be solved firstly to calculate the lateral stretch λ_{lat}. Then, this value is inserted into (63) to compute σ_R. Since (64) possesses the general form $\lambda_{\text{lat}}^2 = g(\lambda_{\text{lat}}^2)$, it can be solved numerically with the fixed point iteration: $\lambda_{\text{lat}(n+1)}^2 = g(\lambda_{\text{lat}(n)}^2)$. In order to provide a suitable starting value $\lambda_{\text{lat}(1)}^2 = 1/\lambda$ was applied. The numerical results for the stress σ_R as function of the axial stretch and the temperature are plotted in Fig. 3.

If the prescribed stretch of the specimen is sufficiently small, the stress is decreasing with increasing temperature. But when the applied stretch becomes larger, the stress is increasing with growing temperature. These effects are the result of the influence of thermal expansion in combination with entropy elasticity.

4.2. Chemical curing reactions and volume changes

In this example, exothermal curing reactions of polymers are discussed which usually take place in combination with chemical volume changes. In this case, the general structure of the hybrid free energy density can be assumed as follows:

$$\varphi = \varphi_{\text{vol}}(p, \theta, q) + \varphi_{\text{iso}}(\hat{\mathbf{E}}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_n, q) \tag{65}$$
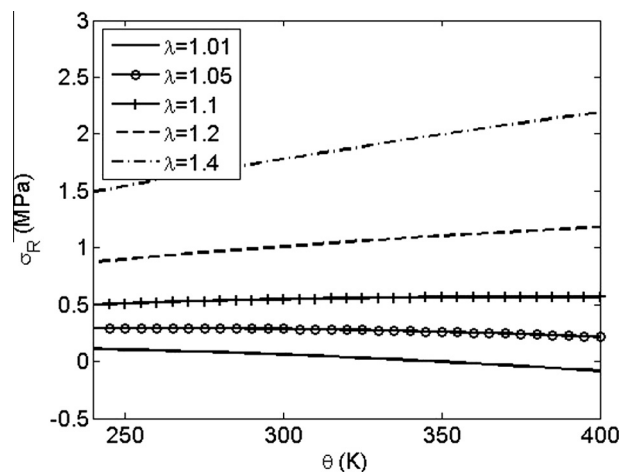

Fig. 3. Numerical simulations of the thermoelastic inversion effect at different stretch values; material parameters: $\mu = 1$ MPa, $\kappa = 3000$ MPa, $\alpha = 6.39 \times 10^{-4}$ K^{-1}, $\theta_0 = 300$ K.

The scalar internal variable $0 \leqslant q \leqslant 1$ is the degree of cure which is introduced to represent the temporal evolution of the chemical curing reaction: $q = 0$ describes the uncured state of the polymer and $q = 1$ is attributed to the completely cured state. The tensorial internal variables $\mathbf{Q}_k$ are introduced to model the thermoviscoelastic mechanical material behaviour of the polymer for arbitrary curing states. The structure of (65) postulates, that the volumetric material behaviour is independent on both the isochoric Green strain tensor $\hat{\mathbf{E}}$ and the viscoelastic internal variables. In the following discussion, only changes in temperature and pressure are studied such that $\hat{\mathbf{E}} = \mathbf{0}$ and $\varphi_{\mathrm{iso}} = 0$ hold for all times. Since the changes in volume of solids and liquids are relatively small, the general structure of (55) can be taken as a basis and extended by the degree of cure-dependent chemical change in volume. To this end, two further empirical material constants β_1 and β_2 are introduced:

$$\varepsilon_{\mathrm{vol}} = \alpha(\theta - \theta_0) - \frac{1}{\kappa}p + \beta_1 q + \beta_2 q^2 \tag{66}$$

The nonlinear dependence of (66) on the degree of cure is motivated by the experimental data plotted in Fig. 4. The material under consideration is an epoxy-based structural adhesive which is applied in the automotive industry to join components of car bodies. The dependence of the chemical volume change on the degree of cure has been measured with internally developed testing equipment and procedures which are based on the principle of Archimedes in combination with differential scanning calorimetry (cf. Kolmeder and Lion, 2010; Kolmeder et al., 2011; Yagimli and Lion, 2011).

In order to compute the volumetric part of the hybrid free energy on the basis of (66), the potential relation (25) is applied in combination with the assumption of $\partial \varphi_{\mathrm{iso}}/\partial p = 0$:

$$\varepsilon_{\mathrm{vol}} = \rho_R \frac{\partial \varphi_{\mathrm{vol}}}{\partial p} = \alpha(\theta - \theta_0) - \frac{1}{\kappa}p + \beta_1 q + \beta_2 q^2 \tag{67}$$

Integration of (67) leads to the expression

$$\varphi_{\mathrm{vol}} = \frac{1}{\rho_R}\left(\alpha(\theta - \theta_0)p - \frac{1}{2\kappa}p^2 + (\beta_1 q + \beta_2 q^2)p + A(\theta, q)\right) \tag{68}$$

in which $A(\theta, q)$ is an integration constant with regard to the pressure. For physical reasons, this function is represented as follows:

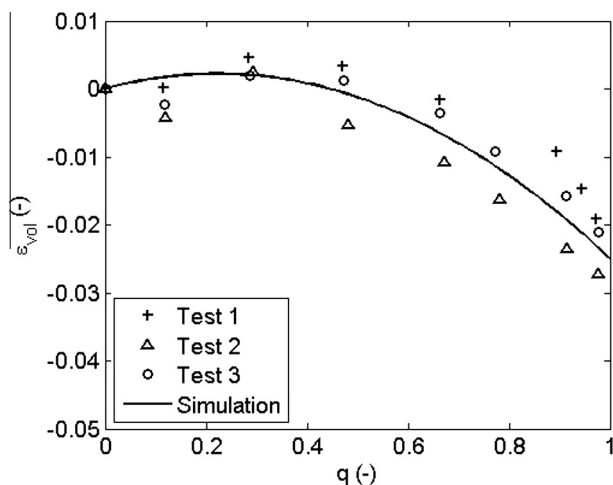$$A = \rho_R h_0 (1 - q) + \rho_R \varphi_0(\theta) \tag{69}$$

Fig. 4. Chemically-induced change in volume of a structural adhesive; material parameters: $\beta_1 = 0.02$, $\beta_2 = -0.045$.

The material constant h_0 is the total reaction enthalpy per unit mass of the curing polymer at zero pressure; the temperature-dependent function $\varphi_0(\theta)$ is related to the isobaric specific heat of the polymer in the completely cured state. In order to satisfy the residual inequality (26), the evolution equation for the degree of cure has to fulfil the following inequality:

$$-\rho_R \frac{\partial \varphi_{\mathrm{vol}}}{\partial q}\dot{q} \geqslant 0 \Rightarrow (\rho_R h_0 - (\beta_1 + 2\beta_2 q)p)\dot{q} \geqslant 0 \tag{70}$$

A thermodynamic consistent curing model is given by the expression

$$\dot{q} = \frac{\rho_R h_0 - (\beta_1 + 2\beta_2 q)p}{\rho_R h_0}f(q, \theta) \tag{71}$$

in which $f(q, \theta) \geqslant 0$ is an appropriate temperature- and degree of cure-dependent curing model (cf. Kamal et al., 1973; Kamal, 1974; Yagimli and Lion, 2011, etc.). In dependence on the sign and the magnitude of the pressure, the degree of cure and the material parameters, the expression $\rho_R h_0 - (\beta_1 + 2\beta_2 q)p$ in (70) and (71) can be positive, negative or zero. The interpretation of this term is as follows: the curing behaviour of a material which exhibits chemical shrinkage, i.e. β_1, $\beta_2 < 0$, can be accelerated when a positive pressure is applied and is decelerated by a negative pressure. If swelling takes place, the opposite holds. For the investigated adhesive, the numerical values $h_0 = 2 \times 10^5$ J/kg, $\rho_R = 1.1 \times 10^3$ kg/m³, $\beta_1 = 0.02$ and $\beta_2 = -0.045$ were experimentally determined such that $\rho_R h_0$ is of the order of 10^8 J/m³. If, in a worst-case scenario, an unrealistic high pressure of 100 MPa in combination with $q = 1$ is assumed, the term $(\beta_1 + 2\beta_2 q)p$ is of the order of 10^6 J/m³. As the most important result of this estimation $(\rho_R h_0 - (\beta_1 + 2\beta_2 q)p)/\rho_R h_0 \approx 1$ holds such that (71) simplifies:

$$\dot{q} = f(q, \theta) \tag{72}$$

There are many standard methods in the literature how to determine nonlinear curing models in the general form of (72) on the basis of differential scanning calorimetry measurements (cf. Yagimli and Lion, 2011 and citations therein).

Now, the isobaric specific heat is computed. If (68) and (69) are combined, the final form of the volumetric part of the hybrid free energy reads as follows:

$$\varphi_{\mathrm{vol}} = \frac{1}{\rho_R}\left(\alpha(\theta - \theta_0)p - \frac{1}{2\kappa}p^2 + (\beta_1 q + \beta_2 q^2)p + \rho_R h_0(1 - q) + \rho_R \varphi_0(\theta)\right) \tag{73}$$

Considering the structure of (65) in combination with (47) the intermediate result

$$c_p \dot{\theta} = -\theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial \theta^2}\dot{\theta} + \left(\frac{\partial \varphi_{\mathrm{vol}}}{\partial q} - \theta \frac{\partial^2 \varphi_{\mathrm{vol}}}{\partial q \partial \theta}\right)\dot{q} \tag{74}$$

is obtained which leads to the following expression when (73) is inserted:

$$c_p \dot{\theta} = -\theta \frac{\partial^2 \varphi_0}{\partial \theta^2}\dot{\theta} + \frac{(\beta_1 + 2\beta_2 q)p - \rho_R h_0}{\rho_R}\dot{q} \tag{75}$$

Taking the discussion with regard to (71) and (72) into account, the following approximation holds:

$$c_p \dot{\theta} = -\theta \frac{\partial^2 \varphi_0}{\partial \theta^2}\dot{\theta} - h_0 \dot{q} \tag{76}$$

Considering (47), the left-hand side of (76), i.e. the term $c_p \dot{\theta} = P_{\mathrm{DSC}}(t)/m$, is the supplied or emitted heat power per unit mass which can be determined with a differential scanning calorimeter during the curing reaction. The second term on the right-hand side of (76) is the time rate of the exothermally emitted

reaction enthalpy per unit mass. The negative sign expresses the fact that the specific enthalpy of the polymer decreases during the chemical reaction. If the glass transition temperature of the polymer is above the temperature at which the curing process takes place, the mobility of the molecules is significantly reduced. In this case, the diffusion of the reactants becomes more and more constrained such that the reaction rate can become extremely small or even zero for $q_0 < 1$. In the completely cured state, i.e. for $q = 1$ when no diffusion control takes place, the reaction rate is zero: $\dot{q} = f(\theta, 1) = 0$. In this situation (76) leads to the following result:

$$c_p = -\theta \frac{\partial^2 \varphi_0}{\partial \theta^2} \tag{77}$$

This relation shows that the function $\varphi_0(\theta)$ determines the isobaric specific heat of the fully cured polymer. It should be noticed that the current approach does not take into account the glass transition.

In order to visualise some fundamental properties of this approach, the following nonlinear evolution equation (cf. Kamal et al., 1973; Kamal, 1974) is assumed to represent the curing reaction in combination with a constant value c_{p0} for the isobaric specific heat:

$$\dot{q} = (A_1 + A_2 q^a)(1-q)^b, \quad A_j = A_{j0} \exp\left(-\frac{B_j}{R\theta}\right) \tag{78}$$

$$c_{p0} = 1620 \text{ J/kg K}, \quad h_0 = 200 \text{ kJ/kg}, \quad A_{10} = A_{20}$$
$$= 4.47 \times 10^8 \text{ s}^{-1}, \quad a = 0.97, \quad b = 1.8$$

$$B_1 = 99.2 \text{ kJ/mol}, \quad B_2 = 88.6 \text{ kJ/mol}, \quad R = 8.314 \text{ J/mol K}$$

The material parameters were determined to describe the curing behaviour of the epoxy-based structural adhesive whose chemically induced volume change is presented in Fig. 4. The simulated responses of the heat power per unit mass P_{DSC}/m were calculated on the basis of (78) in combination with

$$\frac{P_{DSC}}{m} = c_{p0}\dot{\theta} - h_0\dot{q} \tag{79}$$

The curves are depicted in Fig. 5 as function of the temperature for different constant heating rates. The vertical shift of the curves in dependence on the temperature rate is caused by the linearly rate-dependent specific heat term in (79).
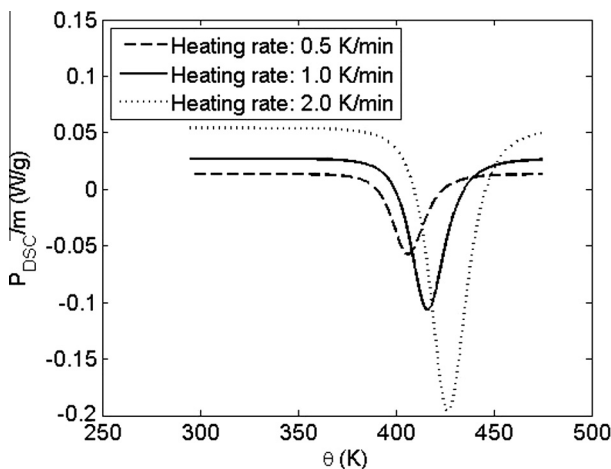
Fig. 5. Simulation of the calorimetric responses of an exothermal curing reaction.

4.3. Glass transition induced changes in the volumetric material behaviour

In this example, the proposed theory is applied to represent the process-dependence of both the isobaric specific heat and the thermal expansion behaviour of polymers in the vicinity of the glass transition. For more information with regard to the glass transition, its interpretation and modelling aspects, the reader is referred to the review article provided by Jäckle (1986) as well as to Davies and Jones (1953). In the current work, the usual interpretation of the glass transition as a kinetic freezing-in thermodynamic non-equilibrium phenomenon is applied (cf. Garden, 2007b; Lion and Yagimli, 2009; Lion and Peters, 2010; Lion et al., 2010; Lion et al., 2011; Tropin et al., 2011; Peters et al., 2011; Richert, 2011, etc.).

If the initial temperature of a glass-forming material is sufficiently high, and it is cooled from this state, the mobility of its molecules is reduced. If the cooling rate is high enough and the final temperature is sufficiently low, crystallization is avoided, the amorphous state is frozen and the material becomes glassy. The characteristic temperature under which glasses remain stable during relevant time scales is the glass transition temperature.

In order to model this type of material behaviour, the hybrid free energy density is assumed to be as follows:

$$\varphi = \varphi_{vol}(p, \theta, \delta) + \varphi_{iso}(\hat{\mathbf{E}}, \theta, \mathbf{Q}_1, \ldots, \mathbf{Q}_n, \delta) \tag{80}$$

The global structure of (80) is similar to that of (65). However, it should be mentioned that the variable δ has a different physical meaning than the variable q in (65) and is determined by a totally different evolution equation. The tensorial variables $\mathbf{Q}_k$ are introduced to represent the thermoviscoelastic material behaviour of the polymer and are driven by the isochoric Green strain tensor. For this part of the model, standard models of finite thermoviscoelasticity can be applied (cf. Lion, 1997; Reese and Govindjee, 1998; Haupt, 2002, etc.). In order to represent the volumetric behaviour of isotropic glass-forming materials under temperature- and pressure-controlled excitations, $\hat{\mathbf{E}} = \mathbf{0}$ and $\varphi_{iso} = 0$ hold and the following assumption is made for the volumetric part of the hybrid free energy density:

$$\varphi_{vol} = \varphi_0 - c_{p0}\theta_0 - s_0(\theta - \theta_0) - (c_{p0} - \beta_0\theta_0)\left(\theta \ln\frac{\theta}{\theta_0} - \theta\right)$$
$$- \frac{\beta_0}{2}(\theta^2 - 2\theta\theta_0 - \theta_0^2) + \frac{\alpha_0}{\rho_R}(\theta - \theta_0)p - \frac{1}{2\rho_R\kappa_0}p^2 + e(\theta$$
$$- \theta_0)\delta + \frac{d}{2}\delta^2 - w\delta p \tag{81}$$

It is an extension of (56) by additional terms whose physical meanings become clear when the volume strain, the isobaric specific heat, the specific entropy and the evolution equation for δ are calculated. The scalars $\varphi_0, c_{p0}, s_0, \beta_0, \alpha_0, \rho_R, \kappa_0, e, d, w$ are material constants. Evaluating (25) under consideration of (81) and $\varphi_{iso} = 0$ leads to:

$$\varepsilon_{vol} = \rho_R \frac{\partial \varphi_{vol}}{\partial p} = \alpha_0(\theta - \theta_0) - \frac{1}{\kappa_0}p - \rho_R w\delta \tag{82}$$

$$s_{vol} = -\frac{\partial \varphi_{vol}}{\partial \theta}$$
$$= s_0 + \beta_0(\theta - \theta_0) + (c_{p0} - \beta_0\theta_0)\ln\frac{\theta}{\theta_0} - \frac{\alpha_0}{\rho_R}p - e\delta \tag{83}$$

Considering the residual inequality (26) and the hybrid free energy (81) a thermodynamically consistent evolution equation for the internal variable δ has to satisfy the condition

$$-\rho_R \frac{\partial \varphi_{vol}}{\partial q}\dot{\delta} \geqslant 0 \Rightarrow -\rho_R(e(\theta - \theta_0) + d\delta - wp)\dot{\delta} \geqslant 0 \tag{84}$$

Accordingly, the evolution of δ can be defined as follows:

$$\dot{\delta}(t) = -A(\theta)(e(\theta - \theta_0) + d\delta - wp) \quad \text{with} \quad A(\theta)$$
$$= A_0 \exp\left(\frac{c_1(\theta - \theta_0)}{c_2 + \theta - \theta_0}\right) \tag{85}$$

The initial condition is $\delta(0) = 0$ and the reciprocal value of $A(\theta)$ is a temperature-dependent relaxation time; c_1, c_2, A_0 are material constants and the ratio $A_0/A(\theta)$ is given by the well-known WLF-equation (cf. Williams et al., 1955). The isobaric specific heat of this model can be computed when (47) is applied under consideration of $\varphi_{\text{iso}} = 0$ and (81):

$$c_{\text{p}} = -\theta \frac{\partial^2 \varphi_{\text{vol}}}{\partial \theta^2} + \frac{1}{\dot{\theta}}\left(\frac{\partial \varphi_{\text{vol}}}{\partial \delta} - \theta \frac{\partial^2 \varphi_{\text{vol}}}{\partial \delta \partial \theta}\right)\dot{\delta}$$
$$\Rightarrow c_{\text{p}} = c_{\text{p}0} + \beta_0(\theta - \theta_0) + \frac{d\delta - wp - e\theta_0}{\dot{\theta}}\dot{\delta} \tag{86}$$

If both the pressure p and the temperature θ are arbitrary functions of time, (82) can be used to calculate the volume strain. In order to derive the isobaric specific heat on the basis of (86), $p = \text{const}$ has to be assumed. Since (82), (83), and (86) depend not exclusively on the current values of p and θ but also on the history-dependent internal state variable δ, the model is thermoviscoelastic.

- In the case of infinitely fast changes in pressure or temperature, (85) leads to $\dot{\delta} = 0$ such that the internal variable is frozen and the material remains in the glassy state. If this process starts from an equilibrium state with $p(0) = 0$, $\theta(0) = \theta_0$ and $\delta(0) = 0$, the internal variable remains zero and the glassy responses of the model can be obtained from (82), (83), and (86):

$$\varepsilon_{\text{vol}}^{\text{glass}} = \alpha_0(\theta - \theta_0) - \frac{1}{\kappa_0}p \tag{87}$$

$$s_{\text{vol}}^{\text{glass}} = s_0 + \beta_0(\theta - \theta_0) + (c_{\text{p}0} - \beta_0\theta_0)\ln\frac{\theta}{\theta_0} - \frac{\alpha_0}{\rho_{\text{R}}}p \tag{88}$$

$$c_{\text{p}}^{\text{glass}} = c_{\text{p}0} + \beta_0(\theta - \theta_0) \tag{89}$$

These relations show that α_0 and $1/\kappa_0$ are the volumetric thermal expansion coefficient and the bulk compliance of the material in the glassy state; $c_{\text{p}0}$ and β_0 are attributed to the isobaric specific heat in the glassy state.

- In the case of infinitely slow changes in the pressure or the temperature, (85) leads to the equilibrium response $\delta^{\text{equil}} = -1/d(e(\theta - \theta_0) - wp)$ for the internal variable. Hence, the material remains in the equilibrium state. Considering (82), (83), and (86) in combination with $p = \text{const}$ for the specific heat calculation, the final result is:

$$\varepsilon_{\text{vol}}^{\text{equil}} = \left(\alpha_0 + \rho_{\text{R}}\frac{we}{d}\right)(\theta - \theta_0) - \left(\frac{1}{\kappa_0} + \rho_{\text{R}}\frac{w^2}{d}\right)p \tag{90}$$

$$s_{\text{vol}}^{\text{equil}} = s_0 + \left(\beta_0 + \frac{e^2}{d}\right)(\theta - \theta_0) + (c_{\text{p}0} - \beta_0\theta_0)\ln\frac{\theta}{\theta_0}$$
$$- \frac{1}{\rho_{\text{R}}}\left(\alpha_0 + \rho_{\text{R}}\frac{ew}{d}\right)p \tag{91}$$

$$c_{\text{p}}^{\text{equil}} = c_{\text{p}0} + \beta_0(\theta - \theta_0) + \frac{d\delta - wp - e\theta_0}{\dot{\theta}}\dot{\delta}^{\text{equil}}$$
$$= c_{\text{p}0} + \beta_0(\theta - \theta_0) + \frac{e^2}{d}\theta \tag{92}$$

The coefficient $1/\kappa_{\text{equil}} = 1/\kappa_0 + \rho_{\text{R}}w^2/d$ is the compliance of the material in the equilibrium state; $\alpha_{\text{equil}} = \alpha_0 + \rho_{\text{R}}we/d$ is the related thermal expansion coefficient. Comparing (89) and (92) it is observed that the temperature dependence of the isobaric specific heat in the glassy range is different from that in the equilibrium range.

In order to illustrate the thermomechanical response behaviour of this model, both the isobaric specific heat (86) and the volume strain (82) were simulated on the basis of (85). To this end, temperature-controlled excitations with piecewise linear sections and pressure-free boundary conditions were assumed and the following equations were evaluated:

$$\dot{\delta} = -A_0 e^{\frac{c_1(\theta - \theta_0)}{c_2 + \theta - \theta_0}}(e(\theta - \theta_0) + d\delta) \tag{93}$$

$$c_{\text{p}} = c_{\text{p}0} + \beta_0(\theta - \theta_0) + \frac{d\delta - e\theta_0}{\dot{\theta}}\dot{\delta} \tag{94}$$

$$\varepsilon_{\text{vol}} = \alpha_0(\theta - \theta_0) - \rho_{\text{R}}w\delta \tag{95}$$

The reference temperature is defined as $\theta_0 = 373$ K and the material parameters of the above listed equations are as follows:

$$\rho_{\text{R}} = 1050 \tfrac{\text{kg}}{\text{m}^3}, \quad c_1 = 17.4, \quad c_2 = 51.6 \text{ K}, \quad A_0 = 0.1 \tfrac{1}{\text{s}},$$
$$e = 7.9 \tfrac{\text{J}}{\text{kg K}}, d = 79.5 \tfrac{\text{J}}{\text{kg}}, \quad c_{\text{p}0} = 10^3 \tfrac{\text{J}}{\text{kg K}},$$
$$\beta_0 = 3.6 \tfrac{1}{\text{K}}, \quad \alpha_0 = 6 \cdot 10^{-4} \tfrac{1}{\text{K}}, \quad w = 1.1 \cdot 10^{-5} \tfrac{\text{m}^2 \text{ J}}{\text{kg N}}$$

Their values were estimated such that the model represents the typical behaviour of polymers near the glass transition.

The evaluation of (93)–(95) was realised with the mathematical software system MATLAB and for the numerical integration of (93) the MATLAB solver ode15 s was used. The results of three simulations are presented in Fig. 6 for the isobaric specific heat and in Fig. 7 for the volume strain. The absolute temperature is plotted on the horizontal axes. All simulations start in the equilibrium state of the material which is characterised by sufficient high temperatures or short relaxation times, i.e. by $1/A(\theta_{\max}) \ll 1$. Hence, $\theta_{\max} = 400$ K was chosen. The related initial condition for the internal variable (93) is $\delta(0) = -e/d(\theta_{\max} - \theta_0)$. In the first segment of the simulation, the temperature was reduced with a constant rate just until the lower value of $\theta_{\min} = 330$ K was reached. Due to $1/A(\theta_{\min}) \gg 1$ the relaxation time of (93) is really large such that the material is in the glassy range. In the simulations, three different cooling rates of 0.1 K/s, 1.0 K/s and 10 K/s were applied to
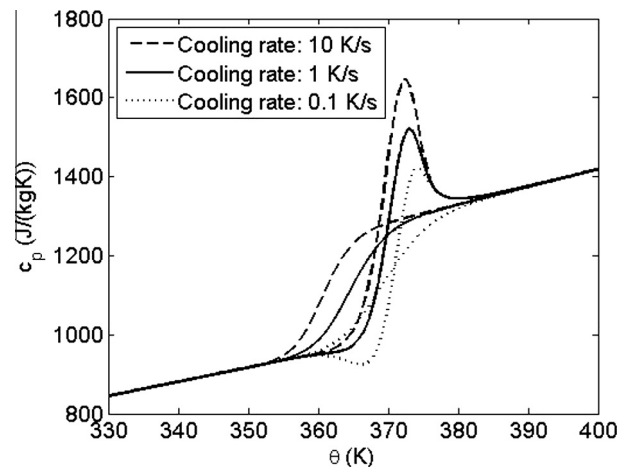

Fig. 6. Simulation of the isobaric specific heat of a model material after cooling with different cooling rates and a heating rate of 10 K/s.
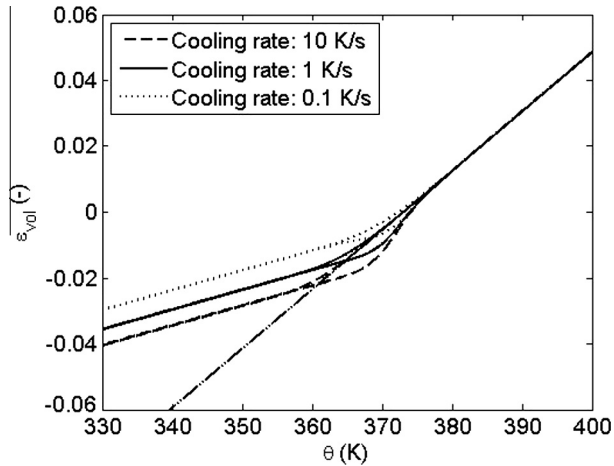
Fig. 7. Simulation of the volume strain of a model material after cooling with different cooling rates and a heating rate of 10 K/s.

transfer the material from the equilibrium to the glassy state. After this, a reheating with a rate of 10 K/s was simulated just until θ_{max} is reached again. For the physical interpretation of the simulated behaviour of specific heat and thermal expansion in the vicinity of the glass transition, the reader is referred to the associated literature and the citations therein (cf. Greiner and Schwarzl, 1986; Jäckle, 1986; Richert, 2011; Peters et al., 2011; Lion et al., 2011, etc.). The non-symmetric response behaviour of the specific heat during cooling and heating as well as the dependence of the maximum of c_p in the reheating segment on the previous cooling rate as depicted in Fig. 6 are known since many decades (cf. Wunderlich et al., 1964; Richert, 2011). The dependence of the volume strain on the temperature process as plotted in Fig. 7 is discussed, for example, in Greiner and Schwarzl (1986) or Peters et al. (2011).

5. Discussion

In this article, a hybrid free energy density $\varphi(\hat{\mathbf{E}}, p, \theta, \ldots)$ is defined and exemplarily applied to model particular properties of elastomers, curing adhesives and glass-forming materials. The term "hybrid" means that it depends on the spherical part of the stress tensor, i.e. on the pressure, and on the isochoric part of the strain tensor which possesses five independent components. It should be mentioned that the mechanical state variable of the Gibbs free energy density $g(\tilde{\mathbf{T}}, \theta, \ldots)$ is the total stress tensor whereas the specific Helmholtz free energy $\psi(\mathbf{E}, \theta, \ldots)$ depends on the total strain tensor (cf. Haupt, 2002, etc.). Therefore, the total number of independent scalar mechanical arguments is identical in all formulations.

When the stress-dependent specific Gibbs free energy is used as thermodynamic potential, the associated caloric quantity is the isobaric specific heat or, alternatively, the time rate of the specific enthalpy at constant pressure. If the function $g(\tilde{\mathbf{T}}, \theta, \ldots)$ is given, the related caloric quantity can be simply derived by partial differentiations in combination with some algebra. As a significant benefit of this approach, the isobaric caloric quantities can be easily measured with the standard technique of differential scanning calorimetry and this data can be used for the parameter identification. Since the specific Gibbs free energy depends on the stress tensor, the thermodynamically conjugated mechanical variable is the strain tensor. It can be directly computed when g is differentiated with respect to the stress. Mechanical material models, in which the strain tensor is the dependent variable, are uncomplicated to use only when they can be solved for the stress tensor. In the case

of infinitesimal strains, such a model has been proposed by Lion et al. (2010) to represent the thermoviscoelastic behaviour of glass-forming materials. But in the case of finite strains or pronounced physical nonlinearities, formulations which are based on the specific Gibbs free energy generally lead to mechanical material models which are no more invertible with regard to the stress tensor.

If the strain-dependent Helmholtz free energy density $\psi(\mathbf{E}, \theta, \ldots)$ is used as thermodynamic potential, the associated caloric quantity is the specific heat at constant volume. In contrast to the specific heat at constant pressure, the isochoric specific heat of solids or liquids cannot be measured with standard calorimetric techniques. If, in spite of this circumstance, experimental data of the isobaric specific heat should be used for the parameter identification, it has to be calculated from the specific Helmholtz free energy. The fact, that this calculation is relatively expensive is an additional aggravating factor. Such a calculation was performed by Lion and Peters (2010) for the complex isobaric and isochoric specific heats in the case of a model of linear thermoviscoelasticity. Since the thermodynamically associated mechanical variable of the strain is the stress tensor, mechanical material models for any type of elastic or inelastic material behaviour are usually formulated on the basis of the specific Helmholtz free energy (e.g. Reese and Govindjee, 1998; Haupt, 2002; Peters et al., 2011, among others which are not cited here). The stress tensor can be directly calculated by differentiation of $\psi(\mathbf{E}, \theta, \ldots)$ with regard to the strain. This concept is applicable for infinitesimal deformations as well as for finite strains and leads to the natural formulation of mechanical material models in which the stress tensor is a functional of strain and temperature.

As a matter of fact, the specific Helmholtz free energy has profound benefits with respect to the representation of mechanical material properties and the Gibbs free energy has essential advantages to represent the caloric material behaviour. In order to combine the advantages of both energy functions, a hybrid free energy density is proposed in this article. The idea is based on the additive decomposition of the stress power (18) into the sum of isochoric and volumetric terms in combination with the Legendre transformation (19) and the evaluation of the Clausius–Duhem inequality (21). The main result is the following energy function together with its potential relations:

$$\varphi = \varphi(\hat{\mathbf{E}}, p, \theta, \ldots) \quad \text{with} \quad \tilde{\tilde{\mathbf{T}}} = \rho_R \left(\frac{\partial \varphi}{\partial \hat{\mathbf{E}}} - \frac{1}{3} \left(\frac{\partial \varphi}{\partial \hat{\mathbf{E}}} \cdot \hat{\mathbf{C}} \right) \hat{\mathbf{C}}^{-1} \right),$$

$$\varepsilon_{vol} = \rho_R \frac{\partial \varphi}{\partial p}, \quad s = -\frac{\partial \varphi}{\partial \theta}$$

In the case of isotropic materials which are loaded with arbitrary pressure and temperature excitations only changes in volume take place such that $\hat{\mathbf{E}} = \mathbf{0}$ and $\tilde{\tilde{\mathbf{T}}} = \mathbf{0}$ hold. Based on the potential relations for the volume strain and the specific entropy in combination with the balance equation of energy, the calorimetric response of the model and the volume strain can be calculated. The experimental investigations which are needed to identify the related material parameters can be carried out with standard techniques such as differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and tests under hydrostatic pressure to measure the bulk modulus. This model structure permits a comparatively simple identification of the bulk behaviour of the material under pressure or temperature excitations. If the hybrid free energy is assumed to be the sum of volumetric and isochoric terms as postulated in (31) the isochoric part of φ can be identified on the basis of temperature-dependent mechanical tests. Since there are numerous constitutive models and mechanical testing techniques in this context, the current article does not discuss this aspect.

In three examples, it has been shown that the approach which is based on the hybrid free energy density in combination with the additive split $\varphi = \varphi_{\mathrm{vol}} + \varphi_{\mathrm{iso}}$ can be easily applied to represent the thermomechanical bulk behaviour of polymers. In order to derive an explicit expression for the stress tensor in the form of (15) it is necessary that the constitutive relation for the volume strain $\varepsilon_{\mathrm{vol}} = F(p, \theta, \ldots)$ can be rearranged in the form of $p = f(\varepsilon_{\mathrm{vol}}, \theta, \ldots)$. If this inversion is impossible or too difficult, for example due to physical nonlinearities, the original relation $\varepsilon_{\mathrm{vol}} = F(p, \theta, \ldots)$ has to be solved numerically.

6. Conclusions

In the future, the promising theory which has been developed in this article should be applied in the context of constitutive modelling and experimental testing of thermomechanical and caloric material properties of polymers. Differential scanning calorimetry in combination with thermomechanical analyses and hydrostatic compression tests are necessary to determine the volumetric part of the constitutive model. As a key result of this work, experimental data of isothermal or non-isothermal calorimetric tests, for example the temperature dependence of the isobaric specific heat or the exothermal heat generation of a curing reaction, can be directly used to identify the temperature-dependent functions of the volumetric part of the material model. In comparison with constitutive approaches which are based on traditional formulations with the Helmholtz or the Gibbs free energy density, the concept of the hybrid free energy density simplifies the representation of caloric and thermomechanically coupled material properties under complex states of stress and strain and varying temperature. It also leads to a better understanding of the term "specific heat" in continuum mechanics.

Acknowledgement

References

Bailey, N.P., Christensen, T., Jakobsen, B., Niss, K., Olsen, N.B., Pedersen, U.R., Schroder, T.B., Dyre, J.C., 2008. Glass-forming liquids: one or more order parameters? Journal of Physics: Condensed Matter 20, 244113.

Bauer, C., Richert, R., Böhmer, R., Christensen, T., 2000. Dynamic thermal expansivity near the glass transition. Journal of Non-Crystalline Solids 262, 261–276.

Boyce, M.C., Socrate, S., Llana, P.-G., 2000. Constitutive model for the finite deformation stress–strain behaviour of poly (ethylene terephthalate) above the glass transition. Polymer 41, 2183–2201.

Davies, R.O., Jones, G.O., 1953. Thermodynamic and kinetic properties of glasses. Advances in Physics 2 (7), 370–410.

Flory, P.J., 1961. Thermodynamic relations for high elastic materials. Transactions of the Faraday Society 57, 829–838.

Garden, J.L., 2007a. Simple derivation of the frequency dependent complex heat capacity. Thermochimica Acta 460, 85–87.

Garden, J.L., 2007b. Macroscopic non-equilibrium thermodynamics in dynamic calorimetry. Thermochimica Acta 452, 85–105.

Greiner, R., Schwarzl, F.R., 1986. Thermal contraction and volume relaxation of amorphous polymers. Rheologica Acta 23, 378–395.

Gutzow, I., Schmelzer, J.W.P., Petroff, B., 2007. The phenomenology of metastable liquids and the glass transition. Journal of Engineering Thermophysics 16, 205–223.

Hartmann, S., Rothe, S., Frage, N., 2013. Electro-thermo-elastic simulation of graphite tools used in SPS processes. In: Altenbach, H., et al. (Eds.), Generalized Continua as Models for Materials, Advanced Structured Materials, vol. 22, pp. 143–161.

Haupt, P., 2002. Continuum Mechanics and Theory of Materials. Springer publication house.

Jäckle, J., 1986. Models of the glass transition. Reports on Progress in Physics 49, 171–231.

Johlitz, M., Scharding, D., Diebels, S., Retka, J., Lion, A., 2010. Modelling of thermo-viscoelastic material behaviour of polyurethane close to the glass transition temperature. Zeitschrift für Angewandte Mathematik und Mechanik 90, 387–398.

Kamal, M.R., 1974. Thermoset characterization for moldability analysis. Polymer Engineering and Science 14, 231–239.

Kamal, M.R., Sourour, S., Ryan, M., 1973. Kinetic and thermal characterization of thermoset cure. Polymer Engineering and Science 13, 59–64.

Kolmeder, S., Lion, A., 2010. On the thermomechanical-chemically coupled behaviour of acrylic bone cements: experimental characterization of material behaviour and modeling approach. Technische Mechanik 30, 195–202.

Kolmeder, S., Lion, A., Landgraf, R., Lion, A., 2011. Thermophysical properties and material modelling of acrylic bone cements used in vertebroplasty. Journal of Thermal Analysis and Calorimetry 105, 705–718.

Laiarinandrasana, L., Besson, J., Lafarge, M., Hochstetter, G., 2009. Temperature dependent mechanical behaviour of PVDF: experiments and numerical modelling. International Journal of Plasticity 25, 1301–1324.

Lion, A., 1997. On the large deformation behaviour of reinforced rubber at different temperatures. Journal of the Mechanics and Physics of Solids 45, 1805–1834.

Lion, A., Peters, J., 2010. 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. Thermochimica Acta 500, 76–87.

Lion, A., Yagimli, B., 2009. On the frequency-dependent specific heat and TMDSC: constitutive modelling based on thermodynamics with internal state variables. Thermochimica Acta 490, 64–74.

Lion, A., Liebl, C., Kolmeder, S., Peters, J., 2010. Representation of the glass-transition in mechanical and thermal properties of glass-forming materials: a three-dimensional theory based on thermodynamics with internal state variables. Journal of the Mechanics and Physics of Solids 58, 1338–1360.

Lion, A., Kolmeder, S., Peters, J., 2011. Simulation of temperature history-dependent phenomena of glass-forming materials based on thermodynamics with internal state variables. Thermochimica Acta 522, 182–193.

Lion, A., Engelhardt, M., Johlitz, M., 2012. Thermomechanical and calorimetric behaviours of supported glass-forming films: a study based on thermodynamics with internal variables. Thin Solid Films 522, 441–451.

Miehe, C., Göktepe, S., Mendez Diez, J., 2009. Finite viscoplasticity of amorphous glassy polymers in the logarithmic strain space. International Journal of Solids and Structures 46, 181–202.

Ogden, R., 1992. On the thermoelastic modelling of rubberlike solids. Journal of Thermal Stresses 15, 533–577.

Peters, J., von Estorff, O., Lion, A., 2011. Description of history-dependent phenomena in polymers: the glass transition in modulus, coefficient of thermal expansion and heat capacity. KGK – Kautschuk Gummi Kunststoffe 64, 40–44.

Reese, S., Govindjee, S., 1998. A theory of finite viscoelasticity and numerical aspects. International Journal of Solids and Structures 35, 3455–3482.

Richert, R., 2011. Heat capacity in the glass transition range modelled on the basis of heterogeneous dynamics. Journal of Chemical Physics 134, 144501.

Treloar, L.R.G., 1975. The Physics of Rubber Elasticity, third ed. Clarendon Press, Oxford.

Tropin, T.V., Schmelzer, J.W.P., Schick, C., 2011. On the dependence of the properties of glasses on cooling and heating rates: I. Entropy, entropy production, and glass transition temperature. Journal of Non-Crystalline Solids 357, 1291–1302.

Williams, M.L., Landel, R.F., Ferry, J.D., 1955. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. Journal of the American Chemical Society 77, 3701–3707.

Wunderlich, B., Bodily, D.B., Kaplan, M.H., 1964. Theory and measurement of the glass-transformation interval of polystyrene. Journal of Applied Physics 35, 95–102.

Yagimli, B., Lion, A., 2011. Experimental investigations and material modelling of curing processes under small deformations. Zeitschrift fur Angewandte Mathematik und Mechanik 91, 342–359.