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Simulation of temperature history-dependent phenomena of glass-forming materials based on thermodynamics with internal state variables

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ABSTRACT

In ref. [1], a profound ansatz for modelling the various phenomena associated with the glass-transition was presented. It extends classical theories, such as the concept of fictive temperature or order parameters, for example, in two ways. Firstly, temperature excitations as well as mechanical loadings are accounted for in a single consistent approach. Secondly, it is not formulated in the θ–p–V space, but rather in the θ–$\underline{\underline{\mathbf{T}}}$–$\underline{\underline{\mathbf{E}}}$ space, taking the tensor character of stress $\underline{\underline{\mathbf{T}}}$ and strain $\underline{\underline{\mathbf{E}}}$ into account. Hence, it is a three-dimensional theory where the basic thermodynamic potential, the Gibbs free energy, depends on the stress tensor, the temperature and a set of internal variables. In the current article, expressions for the enthalpy, the entropy, the thermal expansion and the specific heat are derived. The specific heat and the thermal expansion behaviour are looked at for various temperature excitations. It is shown, that the results are in accord with experimental observations in literature.

1. Introduction

If the temperature of a glass-forming substance is reduced the thermal motion of its molecules is decelerated such that, if crystallization is avoided, it becomes a glass or an amorphous solid. The characteristic temperature under which the material properties of the glass remain stable within larger time frames is commonly denoted as glass transition temperature. As the glassy state of matter is a pronounced non-equilibrium state (see [2–7]), the material properties of glasses change with time through molecular rearrangements and tend to reach an equilibrium state (see [2,8–10]). This is frequently denoted as structural recovery or physical ageing. For more detailed discussions and references in this context the reader is referred to [4]. The behaviour of a glass-forming material in general, and hence especially the occurrence of the glass transition and the associated glass temperature, strongly depend on the ratio of the material's characteristic relaxation times, which are determined by the chemical composition in combination with the prevailing temperature, and a constant, characterizing the experimental time scale. As investigated and modelled by a number of authors, the state of a glass at the end of a quenching or cooling process strongly depends on the temperature rate or, more general, on the entire temperature history (see e.g. [1,8,10–12] or [13]). In order to respond the question whether a glass is stable or not at a certain temperature, the magnitude of the time interval, the physical quantity of interest and the temperature process which was applied to produce the glass play important roles (see e.g. [2]). The same statement holds if the behaviour of a glass in a heating process is to be predicted. The glassy state of matter can also be observed under harmonic temperature excitations at a fixed mean temperature or under harmonic mechanical excitations. This leads to a distinct frequency dependence of the thermomechanical material properties in the vicinity of the glass transition (see [14–20] or [21]). For practical applications, in many glass-forming materials the time-temperature- or frequency-temperature-superposition principle, often associated with WLF- or VFT-shifting factors, can be made use of to take into account the influence of the ratio between material and experimental time scales (see [36,37]).

Glass-forming polymers are applied in various fields in different industries. Rubber products are commonly used above the glass transition temperature whereas other polymer products like gear-wheels or boxes are typically used below it. If the temperature of a technical product undergoes an undesired variation such that the glass transition temperature of the material is reached, the product can fail. During quenching or high-speed cooling in the context of injection moulding processes of molten thermoplastics the glass transition region is passed through. Due to glass transition-induced changes in the thermal expansion behaviour, the specific heat and the mechanical material behaviour, high-speed cooling can lead to residual stresses which influence the durability of the product. In order to quantify glass transition-induced phenomena in the context of the industrial fabrication of polymer components and to

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simulate their influence on the behaviour of the final products, it is enormously helpful to conduct numerical simulations with the finite element method. To this end, three-dimensional constitutive models are required which can represent all relevant material properties in the region of the glass transition. Such models have to consider the tensor character of stress and strain as in solid state physics.

In order to represent the thermal expansion and the calorimetric behaviour of glass-forming substances in dependence on the temperature history, there exist two well-known traditional approaches. In both concepts – besides the conventional state variables temperature and pressure or volume – supplementary state variables are introduced to represent the history-dependent behaviour of glass-forming materials. The first approach is based on the concept of the so-called fictive temperature (e.g. [1,14,22–24] or [25]) and the second one on that of structural order parameters (see e.g. [7,26–30] or [31]). The fictive temperature approach is phenomenologically formulated and does not follow from thermodynamic considerations. The order parameter approach is based on thermodynamics of irreversible processes and uses the Gibbs free energy as thermodynamic potential (see e.g. [28] or [32] and the references therein). Order parameters are introduced as phenomenological measures for the configurational state of the material ([28,31]). In the case of infinitely fast temperature changes the additional state variables are frozen, and in the case of sufficiently slow changes, they possess equilibrium values, which in case of the fictive temperature is the real temperature. From a more general viewpoint, the fictive temperature can be interpreted as a special choice of an order parameter.

In the models described in [28] and [32], the Gibbs free energy has been approximated up to second order terms in the order parameters. In contrast to these models which are formulated using the scalar pressure and the scalar volume as mechanical state variables, the approach developed by the authors in [1] is formulated for the three-dimensional case using stress and strain tensors as mechanical state variables in addition to the temperature and a set of internal state variables. Since each internal state variable can exhibit its own temperature-dependent relaxation time, this approach can take the dynamic heterogeneity of glass-forming materials into account. In comparison with other models, the history-dependence with respect to temperature and mechanical loadings is incorporated in one single holistic approach. The constitutive relations for the entropy and the strain tensor resulting from the constitutive model for the Gibbs free energy are consequences of a stringent evaluation of the second law of thermodynamics in form of the Clausius-Duhem inequality. This inequality also facilitates the formulation of thermodynamical consistent evolution equations which determine the current values of the internal state variables.

The current article is organized as follows. In the next chapter, the fundamental relations of the constitutive model are motivated, shortly explained and summarized. In the third chapter, these equations are evaluated and reformulated for processes with temperature excitations in the time or the frequency domain under constant states of stress as input. In the fourth chapter, numerical simulations of a glass-forming model material are shown. In the fifth chapter, the simulation results are discussed.

2. Basic equations

In Lion and Yagimli [33], Lion and Peters [34] and recently, in a three-dimensional version, in Lion et al. [1], a constitutive approach representing the thermomechanical behaviour of glass-forming materials in the neighbourhood of the glass-transition has been developed. In comparison with classical approaches, in which the specific Gibbs free energy g depends on the pressure p, the temperature θ and a set of internal variables, it depends on the three-dimensional stress tensor $\underline{\underline{\mathbf{T}}}$ in addition to the just mentioned state variables in the current approach. The reason for this choice is the development of a general constitutive theory which considers not only the process-dependent volumetric deformation behaviour of glass-forming materials but also their thermoviscoelastic behaviour under complex three-dimensional states of stress and strain. This extension is needed, for example, for the simulation of fabrication processes in mechanical engineering.

In order to simplify the notation, the symmetric stress tensor $\underline{\underline{\mathbf{T}}}$ is written in Voigt notation

$$\underline{\underline{\mathbf{T}}} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{bmatrix} \quad \rightarrow \quad \underline{\mathbf{T}} = \left[\, T_{11} \quad T_{22} \quad T_{33} \qquad T_{12} \quad T_{23} \quad T_{13} \,\right]^{\mathrm{T}}, \tag{2.1}$$

such that instead of the 3×3 stress tensor $\underline{\underline{\mathbf{T}}}$ the corresponding 6×1 vector representation $\underline{\mathbf{T}}$ in Voigt notation is used. The same is true for the strain tensor $\underline{\underline{\mathbf{E}}}$ and the corresponding Voigt representation $\underline{\mathbf{E}}$. With this notation for the Gibbs free energy

$$g = g(\underline{\mathbf{T}}, \theta, \underline{\alpha}_1, \ldots \underline{\alpha}_m) \tag{2.2}$$

holds, where the internal state variables have been also grouped into 6×1 vectors with

$$\underline{\alpha}_k = \begin{bmatrix} \alpha_{k1} & \alpha_{k2} & \alpha_{k3} & \alpha_{k4} & \alpha_{k5} & \alpha_{k6} \end{bmatrix}^{\mathrm{T}} \tag{2.3}$$

Basis for the development of the constitutive theory is a material in a reference state, which is chosen to be an equilibrium state with constant values of the thermodynamic temperature θ_{ref}, the strain tensor $\underline{\mathbf{E}}_{\mathrm{ref}}$, the stress tensor $\underline{\mathbf{T}}_{\mathrm{ref}}$, the specific entropy per unit mass s_{ref}, the specific Gibbs free energy g_{ref} and the set of m internal variable vectors $\underline{\alpha}_{1\mathrm{ref}}$, $\underline{\alpha}_{2\mathrm{ref}} \ldots$, $\underline{\alpha}_{m\mathrm{ref}}$. If constant values of the stress tensor $\underline{\mathbf{T}}_{\mathrm{ref}}$ and the temperature θ_{ref} are given and held fixed for an infinitely long duration, then all other state variables of the glass-forming material relax asymptotically to time-independent equilibrium values which define the reference state of the model. The vicinity of this state is defined by sufficient small fluctuations in these variables. Since the theory is only valid in a certain neighbourhood of the reference state, extrapolations to the absolute zero-point of the temperature or to extremely large pressures or stresses are not possible. In order to describe the time-dependent material behaviour, a set of perturbation functions $\vartheta(t)$, $\underline{\mathit{\Gamma}}(t)$, $\underline{\mathit{\Sigma}}(t)$, $\eta(t)$, $\mu(t)$ and $\underline{\delta}_k(t)$ is introduced. They vanish in the reference state, such that the current values of the state variables can be written as follows[1,2]:

$$\text{Temperature} \quad \theta(t) = \theta_{\mathrm{ref}} + \vartheta(t) \tag{2.4}$$

$$\text{Strain} \quad \underline{\mathbf{E}}(t) = \underline{\mathbf{E}}_{\mathrm{ref}} + \underline{\mathbf{\Gamma}}(t) \tag{2.5}$$

$$\text{Stress} \quad \underline{\mathbf{T}}(t) = \underline{\mathbf{T}}_{\mathrm{ref}} + \underline{\mathbf{\Sigma}}(t) \tag{2.6}$$

$$\text{Specific entropy} \quad s(t) = s_{\mathrm{ref}} + \eta(t) \tag{2.7}$$

$$\text{Specific Gibbs free energy} \quad g(t) = g_{\mathrm{ref}} + \mu(t) \tag{2.8}$$

$$\text{Internal state variable} \quad \underline{\alpha}_k(t) = \underline{\alpha}_{k\,\mathrm{ref}} + \underline{\delta}_k(t) \tag{2.9}$$

An approximation up to second-order terms in all state variables, hence $\underline{\mathbf{T}}$, θ, $\underline{\alpha}_1, \ldots \underline{\alpha}_m$, is applied to obtain the explicit form of the specific Gibbs free energy per unit mass as the thermodynamic potential. As derived in [1], for isotropic materials it takes

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[1] The Voigt notation is used for the corresponding perturbation functions as well: $\underline{\mathit{\Gamma}} = [\chi_{11}, \chi_{22}, \chi_{33}, 2\chi_{12}, 2\chi_{23}, 2\chi_{31}]^T$, $\underline{\mathit{\Sigma}} = [\tau_{11}, \tau_{22}, \tau_{33}, \tau_{12}, \tau_{23}, \tau_{31}]^T$.

[2] The internal state variables are represented as follows: $\underline{\delta}_k = \begin{bmatrix} \delta_{k1} & \delta_{k2} & \delta_{k3} & \delta_{k4} & \delta_{k5} & \delta_{k6} \end{bmatrix}^T, k = 1, \ldots, m$