RESEARCH ARTICLE

Macromolecular Theory and Simulations
www.mts-journal.de

The Logistic Function in Glass Transition Models of Amorphous Polymers: A Theoretical Framework for Isobaric Cooling Processes

Claudio Corbisieri

Studying the macroscopic-phenomenological behavior of amorphous polymers at glass transition is often subject to limitations because the ordinary differential equations that describe the material behavior require numerical solution. To avoid these limitations, ad-hoc-formulated models of the glass transition have been proposed. However, their scope of application is expected to be limited due to insufficient theoretical foundation. This work establishes a theoretical framework for models that use the logistic function to approximate the macroscopic-phenomenological behavior of amorphous polymers at glass transition. For this purpose, an exactly-solvable Riccati equation is derived within thermodynamics with internal state variables. A closed-form expression in terms of mathematical functions for the temperature derivative of a single internal state variable is the result. This closed-form expression contains the logistic function thus featuring a continuous transition region centered around a pressure and cooling-rate dependent transition temperature. Based on comparison of existing models with the exact solution derived from the Riccati equation, generalized models that approximate the thermal expansion coefficient and heat capacity at glass transition are proposed. This work thus demonstrates the validity of the logistic function in glass transition models of amorphous polymers and provides suggestions as to how existing models can be extended in their applicability.

1. Introduction

At glass transition during isobaric cooling, amorphous polymers feature a continuous transition region in their thermodynamic properties, such as the thermal expansion coefficient and the heat capacity.[1–4] Within the macroscopic-phenomenological theory of the glass transition, this continuous transition region can be described by ad-hoc-formulated models[5–9] as well as models that consist of one or a set of ordinary differential equations (ODE's)[10–20]. As described in the following, these ODE's usually require numerical solution and, unlike ad-hoc-formulated models, do not provide a closed-form expression in terms of mathematical functions. Ad-hoc-formulated models might thus be preferred over models that require numerical solution as is often the case for evaluation of experimental data. To predict both shrinkage and warpage of injection-molded parts, for example, polymer processing simulation software requires a closed-form expression in terms of mathematical functions that describes the pressure-volume-temperature (PVT) behavior of the polymer.[5,21,22] For this purpose, the experimental PVT data typically is fitted by an ad-hoc-formulated model. Without theoretical foundation of such ad-hoc-formulated models, however, their scope of application is expected to be limited. With this in mind, the primary objective of this work is to establish a theoretical framework for selected models that approximate the macroscopic-phenomenological behavior of amorphous polymers at glass transition. As a result, this work could provide a theoretical framework for ad-hoc-formulated models that have been successfully applied for evaluation of experimental data in PVT analysis,[5] differential scanning calorimetry[6] and ellipsometry.[7–9]

Corbisieri et al.[5] proposed a model that approximates the temperature- and pressure-dependent specific volume of amorphous polymers in the equilibrium state, the vitreous state and at glass transition. This model provides the closed-form expression in terms of mathematical functions[23]:

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_p = \Theta_g + \Delta\Theta \times \left[\frac{1}{1+\exp\left(-\theta_3(T-T_g)\right)}\right] \tag{1}$$

The glass transition is modeled using the logistic function.[24,25] The brackets [...] in Equation (1) highlight the normalized logistic function. The properties of this model, such as avoiding

C. Corbisieri
Eastern Switzerland University of Applied Sciences
Institute for Materials Technology and Plastics Processing
Oberseestrasse 10, 8640 Rapperswil, Switzerland
E-mail: claudio.corbisieri@ost.ch

C. Corbisieri
Technische Universität Dresden
Institute of Materials Science
Helmholtzstraße 7, 01069 Dresden, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/mats.202400052

[The legal statement for this article was changed on 15 November 2024 after original online publication.]

DOI: 10.1002/mats.202400052

division of the temperature domain into several intervals and thus eliminating discontinuities at glass transition, are beneficial for polymer processing simulation.[5] Furthermore, systematic and reproducible determination of the glass transition temperature, T_g, is facilitated by fitting the exactly-solvable temperature integral of Equation (1) to the experimental data of the specific volume.[5] Because of the model's ad-hoc-formulation, however, its applicability is expected to be limited. For example, the model does not account for the rate-dependence of the glass transition temperature.[1,2,5]

Lacey et al.[6] proposed the model[26]:

$$c_p = c_{p_g} + \frac{\Delta c_p}{1 + \exp\left(-\mu_3 (T - T_g)\right)} \tag{2}$$

Equation (2) approximates the temperature-dependent specific isobaric heat capacity, c_p, in the equilibrium state, the vitreous state and at glass transition. Since Equations (2) and (1) are formally identical, the model from ref. [6] features the same benefits for evaluation of data of the heat capacity. In contrast to Equation (1), however, Equation (2) was adapted from an ansatz proposed by Hutchinson and Kovacs[12] based on similarity considerations. This ansatz proposed by Hutchinson and Kovacs[12] describes the temporal change of specific enthalpy. Kovacs[13] also proposed a formally identical ansatz to describe the temporal change of specific volume. Consequently, it is expected that a similar adaptation can be found for Equation (1). The model in ref. [5] in part loses its ad-hoc-character, however, only because of similarity considerations but not because of a theoretical foundation within the macroscopic-phenomenological theory of the glass transition.

Thermodynamics with internal state variables could provide such a theoretical foundation. Internal state variables are introduced to account for the non-equilibrium behavior of glass-forming materials both in the vitreous state and at glass transition.[18,27] Even though the number of internal state variables required to describe the non-equilibrium state of glass-forming materials is still debated,[28,29] in principle, any temporal process can be described by solving the ODE's that govern the temporal evolution of the internal state variables. For example in case of the complex heat capacity from periodic perturbation with small temperature-amplitude, an exact solution of the corresponding ODE can be found within thermodynamics with internal state variables.[18–20] In general, however, one or a set of ODE's has to be solved numerically to obtain the dynamic response and thus do not provide a closed-form expression in terms of mathematical functions.[11–17] This includes the dynamic response at glass transition during isobaric cooling.

In addition to thermodynamics with internal state variables, other phenomenological theories exist that account for dissipative effects in the dynamic behavior of continua[18,27]: classical irreversible thermodynamics,[30,31] rational thermodynamics,[32] entropy-free thermodynamics,[33,34] and extended irreversible thermodynamics[35] (a comparison of the individual theories, e.g., in refs. [34–36]). In case of rational thermodynamics, for example, the effect of additional degrees of freedom that a system possesses at non-equilibrium is described in terms of constitutive functionals,[32,37,38] also referred to as memory functionals.[18,34] On the other hand, these additional degrees of freedom are directly accounted for by assigning internal state variables to the Gibbs energy, whose temporal evolution is governed by ODE's.[18,27] Since the glass transition is considered to be a kinetic phenomenon with finite entropy production, thermodynamics with internal state variables offers a suitable and, compared to other theories, often less formal approach to describe the macroscopic-phenomenological behavior of glass-forming materials at glass transition (e.g., refs. [14–18]). Whether the glass transition in the limit of slow cooling could be a thermodynamic phase transition[39] as postulated by Gibbs and DiMarzio[40] to resolve the Kauzmann[41] paradox, however, still is subject of debate.[42–45]

In this work, we derive an exactly-solvable Riccati equation that approximates the macroscopic-phenomenological behavior of amorphous polymers at glass transition during isobaric cooling with constant cooling rate within thermodynamics with internal state variables from: 1) a second-order approximation of the Gibbs energy, 2) a dynamic law in the reduced time domain, 3) a first-order approximation for the reciprocal shift-factor, and 4) the Frenkel–Kobeko–Reiner equation. To the best of our knowledge, no such Riccati equation has been documented in literature so far. A closed-form expression for the temperature derivative of a single internal state variable that contains the logistic function is the result. This work thus demonstrates the validity of the logistic function in glass transition models of amorphous polymers. In addition, suggestions are provided as to how existing models can be extended in their applicability, for example, by incorporating the pressure and cooling-rate dependence of the glass transition temperature. Furthermore, a continuous transition region similar to the glass transition during isobaric cooling can also be found in the reciprocal of the pressure-dependent isothermal compressibility. The findings of this work could therefore lead to a better understanding of the pressure-induced glass transition in future work.

2. Methodology

To derive an ODE that describes the glass transition during isobaric cooling within thermodynamics with internal state variables, the controversial question arises as to how many internal state variables are required to describe the non-equilibrium behavior.[28,29] In this work, only a single internal state variable is considered. This simplification is sufficient for comparison with the models in refs. [5–9].

Another major challenge in thermodynamics with internal state variables lies in formulating ansatzes for the Gibbs energy, dynamic law, and relaxation time.[14–20] The ansatzes chosen in this work are expected to be independent of the non-equilibrium process but only hold within material-dependent limitations, such as a limited temperature and pressure range.

After (Section 2.1) introducing the fundamentals of thermodynamics with internal state variables, the required exactly-solvable Riccati equation is obtained through the key steps: (Section 2.2) formulating ansatzes for the Gibbs energy, dynamic law, and relaxation time, (Section 2.3) identifying the ODE for an isobaric process at constant temperature rate, and (Section 2.4) approximating the ODE using the Frenkel–Kobeko–Reiner equation.

2.1. Fundamentals of Thermodynamics with Internal State Variables

First, the coefficient of isobaric thermal expansion, α_P, and specific isobaric heat capacity, c_P, are derived from the Gibbs potential. To describe the macroscopic-phenomenological behavior of a glass-forming material in the vitreous state and at glass transition, at least one internal state variable, ξ, has to be introduced in addition to the natural state variables, i.e., temperature, T, and pressure, P.[18,27] ξ is representative of an additional degree of freedom that a glass-forming material possesses at non-equilibrium.[18] In principle, ξ could also account for multiple additional degrees of freedom that are mutually dependent and thus manifest themselves as a single internal state variable.[45–47] Considering a homogeneous, isotropic, single-component system with constant mass, the specific Gibbs energy, g, is given by[18]

$$g = g(T(t), P(t), \xi(t)) \tag{3}$$

The specific Gibbs energy depends implicitly on time, t. The temporal derivative of the specific Gibbs energy reads

$$\frac{\mathrm{d}g}{\mathrm{d}t} = \left(\frac{\partial g}{\partial T}\right)_{P,\xi}\frac{\mathrm{d}T}{\mathrm{d}t} + \left(\frac{\partial g}{\partial P}\right)_{T,\xi}\frac{\mathrm{d}P}{\mathrm{d}t} + \left(\frac{\partial g}{\partial \xi}\right)_{T,P}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{4}$$

The partial derivatives of the specific Gibbs energy in Equation (4) correspond to the specific entropy, s, the specific volume, v, and the affinity, Ξ, according to[18]

$$s(T, P, \xi) = -\left(\frac{\partial g}{\partial T}\right)_{P,\xi} \tag{5}$$

$$v(T, P, \xi) = \left(\frac{\partial g}{\partial P}\right)_{T,\xi} \tag{6}$$

$$\Xi(T, P, \xi) = -\left(\frac{\partial g}{\partial \xi}\right)_{T,P} \tag{7}$$

The coefficient of isobaric thermal expansion

$$\alpha_P \equiv \frac{1}{v_P}\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P = \frac{1}{v_P}\left(\left(\frac{\partial v}{\partial T}\right)_{P,\xi} + \left(\frac{\partial v}{\partial \xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P\right) \tag{8}$$

and the specific isobaric heat capacity

$$c_P \equiv T\left(\frac{\mathrm{d}s}{\mathrm{d}T}\right)_P = T\left(\left(\frac{\partial s}{\partial T}\right)_{P,\xi} + \left(\frac{\partial s}{\partial \xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P\right) \tag{9}$$

follow from the total derivative of Equations (6) and (5), respectively, for an isobaric process ($\mathrm{d}P = 0$).[18]

Second, the equilibrium condition of the internal state variable is determined from the equilibrium conditions of the affinity,[17,18,27] i.e.,

$$\Xi^e = -\left(\frac{\partial g}{\partial \xi}\right)^e_{T,P} = 0 \tag{10}$$

$$(\mathrm{d}\Xi)^e = 0 \tag{11}$$

The superscript "e" indicates the equilibrium state of the corresponding mathematical expression. Equation (11) yields the equilibrium condition of the internal state variable[17,18,27]:

$$\xi^e = \xi^e(T, P) \tag{12}$$

In the equilibrium state, the internal state variable depends on the natural state variables.

2.2. Formulation of Ansatzes

2.2.1. Ansatz for the Specific Gibbs Energy

It is assumed that the system under consideration remains in the vicinity of the equilibrium state. The specific Gibbs energy thus follows the well-established truncated Taylor expansion[16,20,48]

$$g(T, P, \xi) \cong g^e + \frac{1}{2}\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}(\xi - \xi^e)^2, \qquad g^e = g(T, P, \xi^e) \tag{13}$$

Because the Taylor expansion is evaluated at the equilibrium state, the first partial derivative of the specific Gibbs energy with respect to the internal state variable (Equation (10)) vanishes in the Taylor expansion.

2.2.2. Ansatz for the Dynamic Law

Typically, a temporal dependence of the internal state variable, ξ, from the affinity, Ξ, is suggested for the dynamic law.[15–19,49–52] This ansatz results from a truncated Taylor expansion evaluated at the equilibrium state, neglecting second-order and subsequent terms.[35] Ansatzes that take second-order and subsequent terms of the Taylor expansion into account can be found in literature.[15,16]

Another ansatz is the concept of reduced time.[53–55] According to this concept, it is assumed that a λ-time scale exists in which the internal state variable follows the linear dynamic law

$$\frac{\mathrm{d}\xi}{\mathrm{d}\lambda} = L\Xi = -L\left(\frac{\partial g}{\partial \xi}\right)_{T,P} \tag{14}$$

L is a phenomenological coefficient.[17–19,49–52] The partial derivative of the specific Gibbs energy with respect to the internal state variable

$$\left(\frac{\partial g}{\partial \xi}\right)_{T,P} = \left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}(\xi - \xi^e) \tag{15}$$

follows from the ansatz of the specific Gibbs energy (Equation (13)). The well-established dynamic law[15,16]

$$\begin{aligned}\frac{\mathrm{d}\xi}{\mathrm{d}t} &= -\frac{\mathrm{d}\lambda}{\mathrm{d}t}L\left(\frac{\partial g}{\partial \xi}\right)_{T,P} \\ &= -\frac{\mathrm{d}\lambda}{\mathrm{d}t}L\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}(\xi - \xi^e) \\ &= -\frac{1}{\tilde{\tau}}(\xi - \xi^e)\end{aligned} \tag{16}$$

is derived from Equation (14) by converting the λ-time scale to the t-time scale and inserting Equation (15). $\tilde{\tau}$ denotes the relaxation time.[15,16]

2.2.3. Ansatz for the Relaxation Time

To develop an ansatz for the relaxation time, the variable χ is introduced. χ corresponds to the reciprocal of the shift-factors of the relaxation time, i.e.,

$$\begin{aligned} \tilde{\tau} &= \tau_r/\chi, \\ \chi &= \chi(T,P,\xi) \end{aligned} \tag{17}$$

Since the factor $\mathrm{d}\lambda/\mathrm{d}t$ in Equation (16) can depend on all natural and internal state variables of the Gibbs potential, in principle, also the relaxation time

$$\tilde{\tau} = \left(\frac{\mathrm{d}\lambda}{\mathrm{d}t} L\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\right)^{-1} = \tilde{\tau}(T,P,\xi) \tag{18}$$

and thus χ depend on temperature, T, pressure, P, and the internal state variable, ξ.[15,16]

In accordance with ref. [11] the reciprocal shift-factor, χ, is an exponential function of η according to

$$\chi = \exp(\eta) \tag{19}$$

Several expressions for the relaxation time and therefore the function η can be found in literature. These expressions were derived from considerations in terms of configurational entropy,[56] activation processes[54] and free volume[13,57] based on the work of[10,11]: Adam and Gibbs[56]; Tool[58]; Narayanaswamy[54]; Macedo and Litovitz[59]; and Doolittle,[60,61] from which also the relaxation time according to Williams–Landel–Ferry[62] or equivalently Vogel–Fulcher–Tammann[63–65] follows. Assuming that the temperature remains within a narrow temperature range, all these expressions can be reduced to a first-order approximation of the temperature- and structure-dependent relaxation time proposed by Kovacs et al. (Equation (17) in ref. [11]). Kovacs et al.[11] incorporated this ansatz for the relaxation time in their macroscopic-phenomenological model, which has successfully been applied to describe a variety of structural recovery phenomena in glass-forming materials referred to as Kovacs signatures.[13,42,66] By adapting this first-order approximation of the relaxation time to the formalism of thermodynamics with internal state variables, we develop the ansatz for the relaxation time from the truncated Taylor expansion[48]

$$\begin{aligned} \eta(T,P,\xi) \cong \eta^{ref} &+ \left(\frac{\partial \eta}{\partial T}\right)^{ref}_{P,\xi}(T-T_r) \\ &+ \left(\frac{\partial \eta}{\partial P}\right)^{ref}_{T,\xi}(P-P_r) \\ &+ \left(\frac{\partial \eta}{\partial \xi}\right)^{ref}_{T,P}(\xi-\xi^e), \\ \eta^{ref} &= \eta(T_r,P_r,\xi^e) \end{aligned} \tag{20}$$

evaluated at the reference temperature, T_r, the reference pressure, P_r, in the vicinity of the equilibrium state. Inserting Equation (20) into Equation (19) leads to the reciprocal shift-factor

$$\begin{aligned} \chi \cong \chi_r &\exp\left(K_T(T-T_r)\right) \\ &\times \exp\left(-K_P(P-P_r)\right) \\ &\times \exp\left(-K_\xi(\xi-\xi^e)\right), \\ \chi_r &= \exp\left(\eta^{ref}\right) \end{aligned} \tag{21}$$

K_T, K_P and K_ξ are material-dependent constant parameters. As required, for the relaxation time follows from insertion of Equation (21) into Equation (17):

$$\begin{aligned} \tilde{\tau} &= \frac{\tau_r}{\chi_r} \exp\left(-K_T(T-T_r)\right) \\ &\quad \times \exp\left(K_P(P-P_r)\right) \\ &\quad \times \exp\left(K_\xi(\xi-\xi^e)\right) \\ &= \tilde{\tau}_r a_T a_P a_\xi \end{aligned} \tag{22}$$

$\tilde{\tau}_r = \tau_r/\chi_r$ corresponds to the relaxation time in the reference state. a_T, a_P and a_ξ denote the shift-factors[57,67]

$$\begin{aligned} a_T(T) &= \exp\left(-K_T(T-T_r)\right), \\ a_P(P) &= \exp\left(K_P(P-P_r)\right), \\ a_\xi(T,P,\xi) &= \exp\left(K_\xi(\xi-\xi^e(T,P))\right) \end{aligned} \tag{23}$$

Comparison of Equation (22) with the relaxation time of both the Kovacs–Aklonis–Hutchinson–Ramos[11] model and the Tool–Narayanaswamy–Moynihan[54,58,68] model suggests that the shift-factor a_ξ represents the structural dependence of the relaxation time $\tilde{\tau}$.[42,66] The departure of the internal state variable from its equilibrium state value, $\xi - \xi^e$, can thus be interpreted as a structural parameter that accounts for the thermodynamic formation history of a glass-forming material similar to the departure from equilibrium δ in ref. [11] or the fictive temperature[54,58,68,69] T_f.

2.3. ODE to Describe an Isobaric Process at Constant Temperature Rate

The ansatzes presented in the previous Section 2.2 are expected to be independent of the non-equilibrium process within material-dependent limitations, such as a limited temperature and pressure range. Therefore, for an isobaric process at pressure P_0 and constant temperature rate $\mathrm{d}T/\mathrm{d}t = \beta_0$, i.e.,

$$\begin{aligned} T(t) &= T_0 + \beta_0(t-t_0), \\ P(t) &= P_0 \end{aligned} \tag{24}$$

the dynamic law (Equation (16)) can be written according to[15,16]

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P = -\frac{1}{\beta_0 \tilde{\tau}}\left(\xi_P - \xi^e_P\right) \tag{25}$$

From Equation (25), we derive the temperature derivative that is required to identify the exactly-solvable Riccati equation:

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P = -\left(\frac{\partial \ln\tilde{\tau}}{\partial\xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P^2 - \left(\left(\frac{\partial \ln\tilde{\tau}}{\partial T}\right)_{P,\xi} + \frac{1}{\beta_0\tilde{\tau}}\right)\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P + \frac{1}{\beta_0\tilde{\tau}}\left(\frac{\partial\xi^e}{\partial T}\right)_P \tag{26}$$

The detailed derivation of Equation (26) can be found in Appendix A.

2.4. Approximating the ODE Using the Frenkel–Kobeko–Reiner Equation

In case of an isobaric process at pressure P_0 and constant cooling rate $\beta_0 < 0$, the Frenkel–Kobeko–Reiner equation[4,15,16,70]

$$\beta_0\tilde{\tau}\big|_{T=T_g} = \text{const} \tag{27}$$

states that the glass transition temperature, T_g, can be defined as the temperature at which the product $\beta_0\tilde{\tau}$ is equal to a material-dependent constant parameter. Inserting Equation (22) into Equation (27) leads to

$$\beta_0\tilde{\tau}_r a_T(T) a_P(P_0)\exp\left(K_\xi\left(\xi_P - \xi_P^e\right)\right)\Big|_{T=T_g} = \text{const} \tag{28}$$

Equation (28) implies that the departure of the internal state variable from its equilibrium state value, $\xi_P - \xi_P^e$, is equal to a material-dependent constant parameter at glass transition temperature. Therefore, this departure can be collected in the parameter $\tilde{\tau}_{r\,\xi}$ according to

$$\tilde{\tau}_{r\,\xi} = \tilde{\tau}_r \exp\left(K_\xi\left(\xi_P - \xi_P^e\right)\right)\Big|_{T=T_g} = \text{const} \tag{29}$$

Using the ansatz of the shift-factor a_T (Equation (23)), Equation (28) thus reads

$$\begin{aligned}\beta_0\tilde{\tau}\big|_{T=T_g} &= \beta_0\tilde{\tau}_{r\,\xi} a_P a_T(T)\Big|_{T=T_g}\\ &= \beta_0\tilde{\tau}_{r\,\xi} a_P \exp\left(-K_T\left(T_g - T_r\right)\right)\\ &= -1/K_\beta\end{aligned} \tag{30}$$

Hence, we assume: In the vicinity of the glass transition, the reciprocal of $\beta_0\tilde{\tau}$,

$$\frac{1}{\beta_0\tilde{\tau}} \cong -K_\beta \tag{31}$$

and the partial derivative of the logarithm of the relaxation time with respect to temperature,[13,71]

$$\left(\frac{\partial \ln\tilde{\tau}}{\partial T}\right)_{P,\xi} \cong -K_T \tag{32}$$

can be approximated by the parameter $-K_\beta$ and the temperature derivative of the logarithm of the shift-factor a_T, i.e., $\mathrm{d}\ln a_T/\mathrm{d}T = -K_T$, respectively.

The partial derivative of the internal state variable in the equilibrium state with respect to temperature is approximated by its temperature-average in the vicinity of the glass transition,[52,72] i.e.,

$$\left(\frac{\partial\xi^e}{\partial T}\right)_P \cong \left\langle\left(\frac{\partial\xi^e}{\partial T}\right)_P\right\rangle = K_\theta \tag{33}$$

because its actual temperature-dependence is unknown. Following

$$\left(\frac{\partial \ln\tilde{\tau}}{\partial\xi}\right)_{T,P} = K_\xi \tag{34}$$

and Equations (31)–(33), we conclude that, in case of an isobaric process at constant cooling rate in the vicinity of the glass transition, Equation (26) can be approximated according to

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P \cong -K_\xi\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P^2 + \left(K_T + K_\beta\right)\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P - K_\beta K_\theta \tag{35}$$

K_β and K_θ are material-dependent constant parameters.

3. Results

By substituting $\zeta_P = (\mathrm{d}\xi/\mathrm{d}T)_P$, Equation (35) reads

$$\left(\frac{\mathrm{d}\zeta}{\mathrm{d}T}\right)_P = C_2\zeta_P^2 + C_1\zeta_P + C_0 \tag{36}$$

Equation (36) is an exactly-solvable Riccati equation with constant parameters C_0, C_1 and C_2.[25] Equation (36) can be separated and solved by integration according to

$$\int \mathrm{d}T = \int \frac{\mathrm{d}\zeta_P}{C_2\zeta_P^2 + C_1\zeta_P + C_0} = T - K_4 \tag{37}$$

K_4 is an integration constant. Only if both conditions

$$\Delta = 4C_2C_0 - C_1^2 < 0 \tag{38}$$

$$\left|\left(2C_2\zeta_P + C_1\right)/\sqrt{|\Delta|}\right| < 1 \tag{39}$$

hold, the exact solution of the Riccati equation

$$\begin{aligned}\zeta_P &= -\frac{\sqrt{C_1^2 - 4C_2C_0}}{2C_2}\\ &\quad\times\tanh\left(\frac{\sqrt{C_1^2 - 4C_2C_0}}{2}\left(T - K_4\right)\right) - \frac{C_1}{2C_2}\\ &= K_1 + \frac{K_2}{1 + \exp\left(-K_3(T - K_4)\right)}\end{aligned} \tag{40}$$

follows from Equation (37).[73–75] The set of parameters are related according to

$$C_2 = -K_\xi = -K_3/K_2 \tag{41}$$

$$C_1 = K_T + K_\beta = K_3(2K_1 + K_2)/K_2 \tag{42}$$

$$C_0 = -K_\beta K_\theta = -K_1 K_3(K_1 + K_2)/K_2 \tag{43}$$

Equation (38) leads to $K_3^2 > 0$, which is fulfilled because of $K_3 \in \mathbb{R}$. Equation (39) limits ζ_P to $K_1 < \zeta_P < K_1 + K_2$. The exact solution of Equation (35) can thus be written as

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P = K_1 + \frac{K_2}{1 + \exp\left(-K_3(T - K_4)\right)} \tag{44}$$

Equation (44) corresponds to the exact solution required for comparison with the models in refs. [5–9]. Equation (44) is the main result of this work.

4. Discussion

The primary objective of this work is to establish a theoretical framework for models that use the logistic function to approximate the macroscopic-phenomenological behavior of amorphous polymers at glass transition. This objective was achieved through the key steps: (Section 4.1) analyzing the exact solution and its connection to the logistic function, (Section 4.2) comparing the exact solution with the models in refs. [5–9], and (Section 4.3) assessing the implications from derivation of the exact solution. The findings of this work are summarized by formulating generalized models to approximate the glass transition during isobaric cooling at constant cooling rate (Section 4.4).

4.1. Analysis of the Exact Solution

Equation (44) is normalized according to

$$\psi = \frac{(\mathrm{d}\xi/\mathrm{d}T)_P - K_1}{K_2} = \frac{1}{1 + \exp\left(-K_3(T - K_4)\right)} \tag{45}$$

ψ corresponds to the normalized logistic function.[24,25] The steepness of the continuous transition region and the location of the inflection point are controlled by the parameter K_3 and K_4, respectively. At temperatures in the vicinity of K_4, the temperature derivative of the internal state variable features a continuous transition region in the temperature domain. The parameter K_4 can thus be interpreted as the transition temperature (**Figure 1**).

The temperature derivative of the internal state variable (Equation (44)) can be found in both the temperature derivative of the specific volume (Equation (8)), i.e.,

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P = \left(\frac{\partial v}{\partial T}\right)_{P,\xi} + K_1\left(\frac{\partial v}{\partial \xi}\right)_{T,P} + \frac{K_2(\partial v/\partial \xi)_{T,P}}{1 + \exp\left(-K_3(T - K_4)\right)} \tag{46}$$

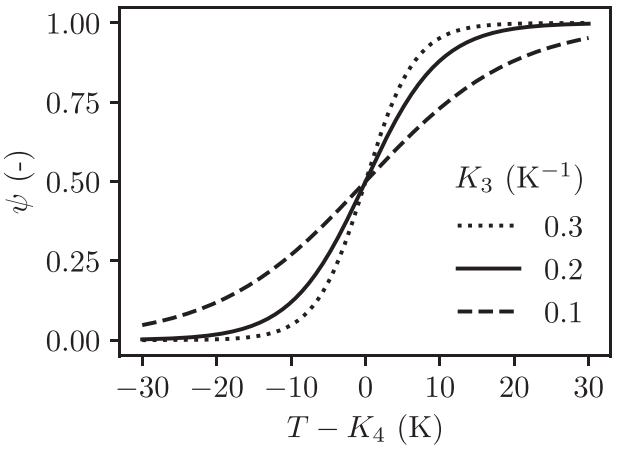

Figure 1. Normalized exact solution, ψ, of the Riccati equation[25] that approximates the macroscopic-phenomenological behavior of amorphous polymers at glass transition during isobaric cooling at constant cooling rate; ψ corresponds to the normalized logistic function[24,25]; T denotes the temperature; the transition temperature K_4 controls the location of the inflection point; K_3 controls the steepness of the continuous transition region; the approximate values of K_3 were taken from data-fits of the model proposed by Corbisieri et al. to experimental data of the amorphous polymer polyethersulfone (PES).[5]

and the product of temperature and temperature derivative of the specific entropy (Equation (9)), i.e.,

$$T\left(\frac{\mathrm{d}s}{\mathrm{d}T}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_{P,\xi} + K_1 T\left(\frac{\partial s}{\partial \xi}\right)_{T,P} + \frac{K_2 T(\partial s/\partial \xi)_{T,P}}{1 + \exp\left(-K_3(T - K_4)\right)} \tag{47}$$

Therefore, a continuous transition region is expected to be found in both the coefficient of isobaric thermal expansion and specific isobaric heat capacity. Experimental studies on the coefficient of isobaric thermal expansion and specific isobaric heat capacity at glass transition during isobaric cooling at constant cooling rate support this conclusion.[1–4]

4.2. Comparison of the Exact Solution with Selected Models

According to the ansatz successfully applied by Corbisieri et al.[5] to model the PVT behavior of amorphous polymers in the equilibrium state, the vitreous state and at glass transition, the parameters Θ_g and $\Delta\Theta$ in Equation (1) are temperature-independent (cf. Equation (9) in ref. [5]). Equation (1) thus reads

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P = \theta_1 + \frac{\theta_2}{1 + \exp\left(-\theta_3(T - T_g)\right)} \tag{48}$$

The parameters θ_1, θ_2 and θ_3 are temperature-independent. Comparison of Equations (48) and (46) suggests that the model in ref. [5] assigns pressure-dependent parameters to both the partial derivative of the specific volume with respect to temperature

$$\left(\frac{\partial v}{\partial T}\right)_{P,\xi} = b_1 \tag{49}$$

and the partial derivative of the specific volume with respect to the internal state variable

$$\left(\frac{\partial v}{\partial \xi}\right)_{T,P} = b_2 \tag{50}$$

Since the partial derivatives in Equations (49) and (50) are continuous and $v = v(T, P, \xi)$ holds, Clairaut's theorem[76] imposes the condition:

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial v}{\partial T}\right)_{P,\xi}\right)_{T,P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial \xi}\right)_{T,P}\right)_{P,\xi} \tag{51}$$

Equations (49) and (50) and thus the ansatz proposed in ref. [5] fulfill this condition.

For systematic and reproducible determination of the glass transition temperature from experimental data of the specific volume, the temperature integral of Equation (48), i.e.,

$$v_P = \theta_1 T + \frac{\theta_2}{\theta_3}\ln\left(1 + \exp\left(\theta_3\left(T - T_g\right)\right)\right) + \theta_4 \tag{52}$$

can be fitted to the experimental data.[5] The parameter θ_4 is an integration constant. Derivation of Equation (46) formally allows the parameters $\theta_1, \ldots, \theta_4$ and T_g to be pressure-dependent. Validation of Equation (52) using the amorphous polymer polyethersulfone (PES) at $P_0 \cong \{10, 40, 80, \ldots, 200\}$ MPa suggests that θ_3 and thus K_3 are constant within a wide range of pressure.[5] Comparison of Equations (48) and (46) also suggests that the parameter K_4 corresponds to the glass transition temperature, i.e., $K_4 = T_g$.

As pointed out in ref. [5], the specific volume according to Equation (52) linearly depends on temperature both in the equilibrium state ($T \gg T_g$) and vitreous state ($T \ll T_g$), which can be interpreted as a first-order approximation of the actual temperature-dependence. An improved model to approximate the temperature-dependence of the specific volume in the equilibrium state and vitreous state follows from an ansatz successfully applied by Bittrich et al.[7] to model the temperature-dependent thickness of thin polymeric films in the equilibrium state, the vitreous state and at glass transition (cf. fit-function $d(T)$ in ref. [7]). Following ref. [7], the specific volume reads

$$v_P = \vartheta_1 T + \frac{\vartheta_2}{2}T^2 + \frac{\vartheta_5}{\vartheta_3^2}\mathrm{Li}_2\left(-\exp\left(\vartheta_3\left(T - T_g\right)\right)\right) + \frac{\vartheta_4 + \vartheta_5 T}{\vartheta_3}\ln\left(1 + \exp\left(\vartheta_3\left(T - T_g\right)\right)\right) + \vartheta_6 \tag{53}$$

The parameters $\vartheta_1, \ldots, \vartheta_6$ are temperature-independent. The Li_2-function corresponds to the dilogarithm function.[7,78] The temperature derivative of Equation (53) can thus be written as

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P = \vartheta_1 + \vartheta_2 T + \frac{\vartheta_4 + \vartheta_5 T}{1 + \exp\left(-\vartheta_3\left(T - T_g\right)\right)} \tag{54}$$

Comparison of Equations (54) and (46) implies that the model in ref. [7] assigns linear temperature functions to both partial derivatives of the specific volume:

$$\left(\frac{\partial v}{\partial T}\right)_{P,\xi} \to b_{11} + b_{12}T \tag{55}$$

$$\left(\frac{\partial v}{\partial \xi}\right)_{T,P} \to b_{21} + b_{22}T \tag{56}$$

However, this assignment appears to be inconsistent with the condition from Clairaut's theorem[76] (Equation (51)). This inconsistency can be resolved, if one assumes that the partial derivatives of the specific volume are approximately referred to the equilibrium state[18]:

$$\left(\frac{\partial v}{\partial T}\right)_{P,\xi} \cong \left(\frac{\partial v}{\partial T}\right)^e_{P,\xi} = b_{11} + b_{12}T \tag{55}$$

$$\left(\frac{\partial v}{\partial \xi}\right)_{T,P} \cong \left(\frac{\partial v}{\partial \xi}\right)^e_{T,P} = b_{21} + b_{22}T \tag{56}$$

This equilibrium state approximation addresses the inconsistency and allows for a consistent interpretation of the ansatz proposed in ref. [7]. Details on the equilibrium state approximation used in Equations (55) and (56) can be found in Appendix B.

In accordance with ref. [7], if both $\vartheta_2 = 0$ and $\vartheta_5 = 0$ hold, Equation (54) and consequently Equation (48) are formally identical to an ad-hoc-formulated model proposed by Dalnoki–Veress et al. (cf. Equation (1) in refs. [8] and [9]). $\vartheta_2 = 0$ and $\vartheta_5 = 0$ result from $b_{12} = 0$ and $b_{22} = 0$, i.e., a truncated Taylor expansion according to Equations (49) and (50). Furthermore, derivation of Equation (46) allows the parameters $\vartheta_1, \ldots, \vartheta_6$ and T_g to be pressure-dependent. Since the studies in refs. [7–9] were conducted at a single pressure, no conclusions about the pressure-dependence of the parameters $\vartheta_1, \ldots, \vartheta_6$ and T_g can be drawn from this comparison.

Similar to the ansatz proposed in ref. [7], Lacey et al.[6] successfully applied Equation (2) to model the specific isobaric heat capacity in the equilibrium state, the vitreous state and at glass transition using an ansatz with linear temperature-dependence of the specific isobaric heat capacity in the equilibrium state and vitreous state (cf. Equation (52) in ref. [6]). Equation (2) thus reads

$$c_P = \mu_1 + \mu_2 T + \frac{\mu_4 + \mu_5 T}{1 + \exp\left(-\mu_3\left(T - T_g\right)\right)} \tag{57}$$

The parameters $\mu_1, \ldots, \mu_5$ are temperature-independent. By comparing Equations (57) and (47), it is evident that the model in ref. [6] assigns the truncated Taylor expansion in the temperature domain to the products of temperature and partial derivative of the specific entropy, neglecting second-order and subsequent terms:

$$T\left(\frac{\partial s}{\partial T}\right)_{P,\xi} \cong T\left(\frac{\partial s}{\partial T}\right)^e_{P,\xi} = B_{11} + B_{12}T \tag{58}$$

$$T\left(\frac{\partial s}{\partial \xi}\right)_{T,P} \cong T\left(\frac{\partial s}{\partial \xi}\right)^e_{T,P} = B_{21} + B_{22}T \tag{59}$$

Consequently, the ansatz proposed in ref. [6] implies that the partial derivatives of the specific entropy are approximately referred

to the equilibrium state (Appendix C).[18] No information on the pressure-dependence of the parameters $\mu_1, \ldots, \mu_5$ and T_g can be obtained from the model in ref. [6]. Comparison of Equations (57) and (47) confirms that the parameter K_4 can be interpreted as the glass transition temperature, i.e., $K_4 = T_g$.

4.3. Implications from Derivation of the Exact Solution

From comparison of the exact solution with the models in refs. [5–9] (Section 4.2) follows that the parameter K_4 corresponds to the pressure-dependent glass transition temperature, i.e., $K_4 = T_g$. Based on Equation (30), we conclude that the rate-dependence of the glass transition temperature during isobaric cooling at constant cooling rate ($\beta_0 < 0$) can be approximated by

$$T_g(P_0, \beta_0) = T_r + \frac{1}{K_T} \ln\left(\frac{\beta_0}{\tilde{\beta}}\right) \tag{60}$$

$$\tilde{\beta}(P_0) = -\frac{1}{K_\beta \tilde{\tau}_{r\xi} a_P} < 0 \tag{61}$$

Equation (60) is identical to an empirical equation reported by Greiner and Schwarzl[1] as well as Schwarzl and Zahradnik[2] (cf. Equation (1) in ref. [1] and Equation (13) in ref. [2]). Equation (60) was successfully applied to approximate the rate-dependence of the glass transition temperature of several amorphous polymers, such as polycarbonate (PC) and polystyrene (PS), measured during isobaric cooling at constant rate in the order of $-\beta_0 \cong 0.01 \ldots 1\ \mathrm{K\,min^{-1}}$. This finding supports the conclusion that Equations (31) and (32) are suitable approximations to model the macroscopic-phenomenological behavior of amorphous polymers at glass transition during isobaric cooling at constant cooling rate.

The pressure and cooling-rate dependent terms of the glass transition temperature in Equation (60) are separated according to

$$T_g(P_0, \beta_0) = T_{g\,P}(P_0) + \frac{1}{K_T} \ln|\beta_0| \tag{62}$$

$$T_{g\,P}(P_0) = T_r + \frac{1}{K_T} \ln\left(K_\beta \tilde{\tau}_{r\xi} a_P\right) \tag{63}$$

In accordance with refs. [10–13], the material-dependent parameter K_T, which controls the cooling-rate dependence of the glass transition temperature, is determined as follows:

$$\left(\frac{\mathrm{d}T_g}{\mathrm{d}\ln|\beta_0|}\right)_P = \frac{1}{K_T} \tag{64}$$

Values of the parameter range from $K_T \cong 0.1 \ldots 1\ \mathrm{K^{-1}}$ for most glass-forming materials.[10] The higher the absolute value of the cooling rate $|\beta_0|$ at pressure P_0, the higher the glass transition temperature T_g at the same pressure P_0. Because of the Taylor approximation for the relaxation time in Equation (20), however, it is expected that both Equations (60) and (62) only apply within a limited material-dependent range of cooling rates. Consequently, the value of the parameter K_T might not be unique but depends on the glass transition temperature found under the cooling rate $\tilde{\beta}$.

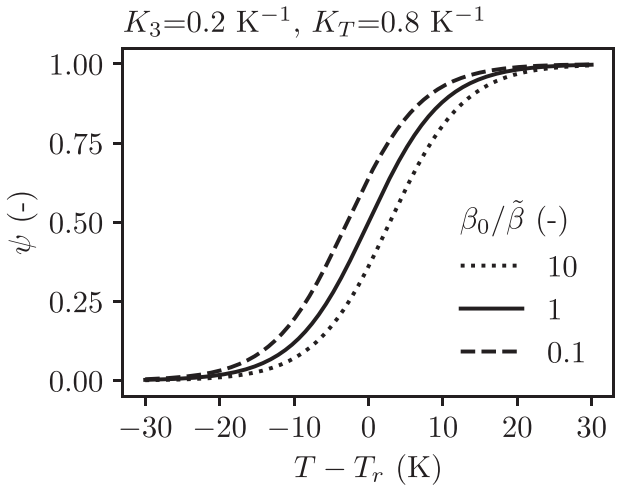

Figure 2. Normalized exact solution, ψ, at several cooling rates β_0; T_r corresponds to the glass transition temperature found under the cooling rate $\tilde{\beta}$; K_T controls the cooling-rate dependence of the glass transition temperature; the value of K_T approximately corresponds to the values reported by Greiner and Schwarzl as well as Schwarzl and Zahradnik for several amorphous polymers, such as polycarbonate (PC) and polystyrene (PS).[1,2]

Substituting the pressure and cooling-rate dependent glass transition temperature T_g (Equation (60)) into the parameter K_4 of the exact solution (Equation (44)) yields the generalization of the exact solution

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P = K_1 + \frac{K_2}{1 + \exp\left(-K_3\left(T - T_r - K_T^{-1}\ln(\beta_0/\tilde{\beta})\right)\right)} \tag{65}$$

In accordance with Equation (45), the normalization of Equation (65) thus reads

$$\psi = \frac{1}{1 + \exp\left(-K_3\left(T - T_r - K_T^{-1}\ln(\beta_0/\tilde{\beta})\right)\right)} \tag{66}$$

As is implied by Equation (66), the cooling rate β_0 affects the location of the inflection point of ψ but not the steepness of the continuous transition region (**Figure 2**).

4.4. Generalized Models to Approximate the Glass Transition During Isobaric Cooling at Constant Cooling Rate

The findings of this work are summarized by formulating generalized models that approximate 1) the coefficient of isobaric thermal expansion and 2) the specific isobaric heat capacity at glass transition during isobaric cooling at pressure P_0 with constant cooling rate $\beta_0 < 0$:

1) Based on Equation (65) and the equilibrium state approximation of the partial derivatives of the specific volume, i.e.,

$$\left(\frac{\partial v}{\partial T}\right)_{P,\xi} \cong \left(\frac{\partial v}{\partial T}\right)^e_{P,\xi} \tag{67}$$

$$\left(\frac{\partial v}{\partial \xi}\right)_{T,P} \cong \left(\frac{\partial v}{\partial \xi}\right)^e_{T,P} \tag{68}$$

we propose the generalized ansatz to model the temperature derivative of the specific volume:

$$\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P \cong \frac{\Delta\Theta(T, P_0)}{1+\exp\left(-K_3\left(T - T_r - K_T^{-1}\ln\left(\beta_0/\tilde{\beta}(P_0)\right)\right)\right)} + \Theta_g(T, P_0) \tag{69}$$

As in Equation (1), Θ_g corresponds to the temperature derivative of the specific volume in the vitreous state at temperatures sufficiently below the pressure and cooling-rate dependent glass transition temperature, i.e., $T \ll T_g$. In the equilibrium state, i.e., $T \gg T_g$, the temperature derivative of the specific volume reads $(\mathrm{d}v/\mathrm{d}T)_P^e = \Theta_g + \Delta\Theta$. $\Delta\Theta$ corresponds to the contribution of the internal state variable to the temperature derivative of the specific volume. In case the temperature integral of Equation (69) provides a closed-form expression in terms of mathematical functions, also the coefficient of isobaric thermal expansion

$$\alpha_P \equiv \frac{1}{v_P}\left(\frac{\mathrm{d}v}{\mathrm{d}T}\right)_P \tag{8}$$

can be written as a closed-form expression in terms of mathematical functions.

2) Based on Equation (65) and the equilibrium state approximation of the partial derivatives of the specific entropy, i.e.,

$$\left(\frac{\partial s}{\partial T}\right)_{P,\xi} \cong \left(\frac{\partial s}{\partial T}\right)_{P,\xi}^e \tag{70}$$

$$\left(\frac{\partial s}{\partial \xi}\right)_{T,P} \cong \left(\frac{\partial s}{\partial \xi}\right)_{T,P}^e \tag{71}$$

we propose the generalized ansatz to model the specific isobaric heat capacity:

$$c_P \cong \frac{\Delta c_P(T, P_0)}{1+\exp\left(-K_3\left(T - T_r - K_T^{-1}\ln\left(\beta_0/\tilde{\beta}(P_0)\right)\right)\right)} + c_{Pg}(T, P_0) \tag{72}$$

In accordance with Equation (2), c_{Pg} denotes the specific isobaric heat capacity in the vitreous state at temperatures sufficiently below the pressure and cooling-rate dependent glass transition temperature, i.e., $T \ll T_g$. In the equilibrium state, i.e., $T \gg T_g$, the specific isobaric heat capacity reads $c_P^e = c_{Pg} + \Delta c_P$. Δc_P corresponds to the contribution of the internal state variable to the specific isobaric heat capacity. In contrast to the coefficient of isobaric thermal expansion, a closed-form expression in terms of mathematical functions is obtained for the specific isobaric heat capacity without the requirement of an additional step of integration.

The generalized models (Equations (69) and (72)) serve as template for potential adaptation of existing models that use the logistic function to approximate the macroscopic-phenomenological behavior of amorphous polymers at glass transition. For example, incorporating the cooling-rate dependence of the glass transition temperature from Equation (69) into the model proposed in ref. [5] could extend the model's scope of application without compromising its theoretical foundation within thermodynamics with internal state variables. Equations (69) and (72) are expected to hold for a homogeneous, isotropic, single-component system with constant mass that is subject to an isobaric process at constant cooling rate in the vicinity of the glass transition within the limitations of the assumptions:

- a single internal state variable sufficiently captures the non-equilibrium behavior (Equation (3)),
- the system remains in the vicinity of the equilibrium state (Equation (13)),
- a reduced time scale exists in which the internal state variable follows a linear dynamic law (Equation (14)),
- the temperature and pressure remain in the vicinity of the reference temperature, T_r, and reference pressure, P_r, respectively (Equation (20)),
- the product of cooling rate and relaxation time can be approximated by the constant parameter of the Frenkel–Kobeko–Reiner equation (Equation (31)),
- the partial derivative of the logarithm of the relaxation time with respect to temperature can be approximated by the temperature derivative of the logarithm of the shift-factor a_T (Equation (32)), and
- the partial derivative of the internal state variable in the equilibrium state with respect to temperature can be approximated by its temperature-average (Equation (33)).

Consequently, the parameters of a constitutive model derived from the generalizations (Equations (69) and (72)) might not be unique but depend on the range of temperatures, pressures and cooling rates to which the constitutive model is fitted. Depending on the temperature-dependence of the parameters Θ_g, $\Delta\Theta$, c_{Pg} and Δc_P, the equilibrium state approximation of the partial derivatives according to Equations (67) and (68) or Equations (70) and (71) is implied. The temperature- and pressure-dependence of Θ_g, $\Delta\Theta$, c_{Pg} and Δc_P as well as the pressure-dependence of $\tilde{\beta}$ is expected to be material-dependent. Furthermore, the parameters K_3 and K_T are expected to be constant within a limited material-dependent range of pressure.

5. Conclusion

An exactly-solvable Riccati equation that approximates the macroscopic-phenomenological behavior of amorphous polymers at glass transition can be derived within thermodynamics with internal state variables (Equation (35)). The exact solution of the Riccati equation contains the logistic function (Equation (44)). Based on comparison of the exact solution with models successfully applied in PVT analysis,[5] differential scanning calorimetry,[6] and ellipsometry,[7–9] generalized models that approximate the coefficient of isobaric thermal expansion and the specific isobaric heat capacity at glass transition during isobaric cooling with constant cooling rate are proposed (Equations (69) and (72)). These generalized models provide a theoretical framework for models that use the logistic function to approximate the macroscopic-phenomenological behavior of amorphous polymers at glass transition. To establish such a theoretical framework was the primary objective of this work.

This work not only demonstrates the validity of the logistic function in glass transition models of amorphous polymers, but also provides suggestions as to how existing models can be extended in their applicability. Based on the generalized models (Equations (69) and (72)), potential adaptation of existing models such as in refs. [5–9] can include: 1) addressing the temperature-dependence of the parameters in the equilibrium state and vitreous state, 2) exploring the pressure-dependence of the parameters, and 3) incorporating the pressure and cooling-rate dependence of the glass transition temperature. To evaluate the dependence of the parameters on the experimental conditions, a constitutive model derived from the generalizations (Equations (69) and (72)) should be fitted to experimental data of the specific volume and specific entropy, respectively, obtained during isobaric cooling in a wide range of temperatures, pressures or cooling rates.

A continuous transition region similar to the glass transition during isobaric cooling can also be found in the reciprocal of the pressure-dependent isothermal compressibility.[45,79–81] Therefore, the methodology developed in this work will be adapted to isothermal processes at constant compression rate in future work. This adaptation could clarify whether the methodology developed in this work also provides a theoretical framework to assess the glass transition during isothermal compression. A relation between the compression rate and the relaxation time similar to the Frenkel–Kobeko–Reiner equation is expected to hold at the glass transition pressure, P_g.[82] The results from this and future work could thus lead to ansatzes with remarkable modeling capability and a deeper understanding of the glass transition in amorphous polymers in the temperature- and pressure-domain.

Appendix A: Derivation of the Ordinary Differential Equation

From the dynamic law

$$\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P = -\frac{1}{\beta_0\tilde{\tau}}\left(\xi_P - \xi_P^e\right) \tag{25}$$

the temperature derivative

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P = \frac{1}{\beta_0\tilde{\tau}}\left(\xi_P - \xi_P^e\right)\left(\frac{\mathrm{d}\ln\tilde{\tau}}{\mathrm{d}T}\right)_P - \frac{1}{\beta_0\tilde{\tau}}\left(\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P - \left(\frac{\mathrm{d}\xi^e}{\mathrm{d}T}\right)_P\right) \tag{A1}$$

follows. Insertion of

$$\frac{1}{\beta_0\tilde{\tau}}\left(\xi_P - \xi_P^e\right) = -\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P \tag{A2}$$

and

$$\left(\frac{\mathrm{d}\xi^e}{\mathrm{d}T}\right)_P = \left(\frac{\partial\xi^e}{\partial T}\right)_P \tag{A3}$$

into Equation (A1) leads to

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P = -\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P\left(\frac{\mathrm{d}\ln\tilde{\tau}}{\mathrm{d}T}\right)_P - \frac{1}{\beta_0\tilde{\tau}}\left(\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P - \left(\frac{\partial\xi^e}{\partial T}\right)_P\right) \tag{A4}$$

The total derivative of the logarithm of the relaxation time reads

$$\mathrm{d}\ln\tilde{\tau} = \left(\frac{\partial\ln\tilde{\tau}}{\partial T}\right)_{P,\xi}\mathrm{d}T + \left(\frac{\partial\ln\tilde{\tau}}{\partial P}\right)_{T,\xi}\mathrm{d}P + \left(\frac{\partial\ln\tilde{\tau}}{\partial\xi}\right)_{T,P}\mathrm{d}\xi \tag{A5}$$

In case of an isobaric process ($\mathrm{d}P = 0$), for Equation (A5) follows

$$\left(\frac{\mathrm{d}\ln\tilde{\tau}}{\mathrm{d}T}\right)_P = \left(\frac{\partial\ln\tilde{\tau}}{\partial T}\right)_{P,\xi} + \left(\frac{\partial\ln\tilde{\tau}}{\partial\xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P \tag{A6}$$

Inserting Equation (A6) into Equation (A4) yields

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P = -\left(\left(\frac{\partial\ln\tilde{\tau}}{\partial T}\right)_{P,\xi} + \left(\frac{\partial\ln\tilde{\tau}}{\partial\xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P\right)\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P - \frac{1}{\beta_0\tilde{\tau}}\left(\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P - \left(\frac{\partial\xi^e}{\partial T}\right)_P\right) \tag{A7}$$

From rearranging Equation (A7), the required temperature derivative is obtained:

$$\left(\frac{\mathrm{d}^2\xi}{\mathrm{d}T^2}\right)_P = -\left(\frac{\partial\ln\tilde{\tau}}{\partial\xi}\right)_{T,P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P^2 - \left(\left(\frac{\partial\ln\tilde{\tau}}{\partial T}\right)_{P,\xi} + \frac{1}{\beta_0\tilde{\tau}}\right)\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right)_P + \frac{1}{\beta_0\tilde{\tau}}\left(\frac{\partial\xi^e}{\partial T}\right)_P \tag{26}$$

Appendix B: Equilibrium State Approximation of the Partial Derivatives of the Specific Volume

The partial derivatives of the specific volume referred to the equilibrium state

$$\left(\frac{\partial\nu}{\partial T}\right)_{P,\xi}^e(T,P) = \left(\frac{\partial\nu}{\partial T}\right)_{P,\xi}(T,P,\xi^e(T,P)) = \left(\frac{\partial}{\partial T}\left(\frac{\partial g^e}{\partial P}\right)_T\right)_P + \left(\frac{\partial^2 g}{\partial\xi^2}\right)_{T,P}^e\left(\frac{\partial\xi^e}{\partial P}\right)_T\left(\frac{\partial\xi^e}{\partial T}\right)_P \tag{B1}$$

$$\left(\frac{\partial\nu}{\partial\xi}\right)_{T,P}^e(T,P) = \left(\frac{\partial\nu}{\partial\xi}\right)_{T,P}(T,P,\xi^e(T,P)) = -\left(\frac{\partial^2 g}{\partial\xi^2}\right)_{T,P}^e\left(\frac{\partial\xi^e}{\partial P}\right)_T \tag{B2}$$

follow from applying Equation (6) to the ansatz of the specific Gibbs energy (Equation (13)). The mixed partial derivative

$$\left(\frac{\partial}{\partial\xi}\left(\frac{\partial\nu}{\partial T}\right)_{P,\xi}^e\right)_{T,P} = 0 \tag{B3}$$

is always equal to zero. On the other hand, the mixed partial derivative

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial\nu}{\partial\xi}\right)_{T,P}^e\right)_P = -\left(\frac{\partial^2 g}{\partial\xi^2}\right)_{T,P}^e\left(\frac{\partial}{\partial T}\left(\frac{\partial\xi^e}{\partial P}\right)_T\right)_P - \left(\frac{\partial}{\partial T}\left(\frac{\partial^2 g}{\partial\xi^2}\right)_{T,P}^e\right)_P\left(\frac{\partial\xi^e}{\partial P}\right)_T \tag{B4}$$

is equal to zero and thus equal to Equation (B3), only if the condition

$$\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\left(\frac{\partial}{\partial T}\left(\frac{\partial \xi^e}{\partial P}\right)_T\right)_P = -\left(\frac{\partial}{\partial T}\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\right)_P\left(\frac{\partial \xi^e}{\partial P}\right)_T \tag{B5}$$

holds. No a priori reason appears to exist within thermodynamics with internal state variables that requires the condition (B5) to be fulfilled at all times. The macroscopic behavior of the glass-forming material thus determines whether the equality

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial \nu}{\partial T}\right)^e_{P,\xi}\right)_{T,P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \nu}{\partial \xi}\right)^e_{T,P}\right)_P = 0 \tag{B6}$$

or the inequality

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial \nu}{\partial T}\right)^e_{P,\xi}\right)_{T,P} \neq \left(\frac{\partial}{\partial T}\left(\frac{\partial \nu}{\partial \xi}\right)^e_{T,P}\right)_P \tag{B7}$$

applies.

Appendix C: Equilibrium State Approximation of the Partial Derivatives of the Specific Entropy

The partial derivatives of the specific entropy referred to the equilibrium state

$$\left(\frac{\partial s}{\partial T}\right)^e_{P,\xi}(T,P) = \left(\frac{\partial s}{\partial T}\right)_{P,\xi}(T,P,\xi^e(T,P)) = -\left(\frac{\partial^2 g^e}{\partial T^2}\right)_P - \left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\left(\frac{\partial \xi^e}{\partial T}\right)^2_P \tag{C1}$$

$$\left(\frac{\partial s}{\partial \xi}\right)^e_{T,P}(T,P) = \left(\frac{\partial s}{\partial \xi}\right)_{T,P}(T,P,\xi^e(T,P)) = \left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\left(\frac{\partial \xi^e}{\partial T}\right)_P \tag{C2}$$

follow from applying Equation (5) to the ansatz of the specific Gibbs energy (Equation (13)). The mixed partial derivative

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial s}{\partial T}\right)^e_{P,\xi}\right)_{T,P} = 0 \tag{C3}$$

is always equal to zero. On the other hand, the mixed partial derivative

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial \xi}\right)^e_{T,P}\right)_P = \left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\left(\frac{\partial^2 \xi^e}{\partial T^2}\right)_P + \left(\frac{\partial}{\partial T}\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\right)_P\left(\frac{\partial \xi^e}{\partial T}\right)_P \tag{C4}$$

is equal to zero and thus equal to Equation (C3), only if the condition

$$\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\left(\frac{\partial^2 \xi^e}{\partial T^2}\right)_P = -\left(\frac{\partial}{\partial T}\left(\frac{\partial^2 g}{\partial \xi^2}\right)^e_{T,P}\right)_P\left(\frac{\partial \xi^e}{\partial T}\right)_P \tag{C5}$$

holds. No a priori reason appears to exist within thermodynamics with internal state variables that requires the condition (C5) to be fulfilled at all times. The macroscopic behavior of the glass-forming material thus determines whether the equality

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial s}{\partial T}\right)^e_{P,\xi}\right)_{T,P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial \xi}\right)^e_{T,P}\right)_P = 0 \tag{C6}$$

or the inequality

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial s}{\partial T}\right)^e_{P,\xi}\right)_{T,P} \neq \left(\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial \xi}\right)^e_{T,P}\right)_P \tag{C7}$$

applies.

Acknowledgements

Results of this work were obtained by the author as visiting scientist at the Leibniz-Institut für Polymerforschung Dresden e. V. The author would like to thank Markus Stommel, Leibniz-Institut für Polymerforschung Dresden e. V., and Frank Ehrig, Eastern Switzerland University of Applied Sciences, who supported the author's visit at the Leibniz-Institut für Polymerforschung Dresden e. V. as visiting scientist. The author would also like to thank Markus Stommel and Lars Bittrich, Leibniz-Institut für Polymerforschung Dresden e. V., as well as Cornelia Breitkopf, Technische Universität Dresden, for their comments on the draft of this publication.

Conflict of Interest

The author declares no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords

amorphous polymer, glass transition, heat capacity, logistic function, thermal expansion coefficient

Received: June 13, 2024
Revised: August 26, 2024
Published online: September 25, 2024

[1] R. Greiner, F. R. Schwarzl, *Rheol. Acta* **1984**, *23*, 378.
[2] F. R. Schwarzl, F. Zahradnik, *Rheol. Acta* **1980**, *19*, 137.
[3] P. Badrinarayanan, W. Zheng, Q. Li, S. L. Simon, *J. Non-Cryst. Solids* **2007**, *353*, 2603.
[4] J. E. K. Schawe, *J. Chem. Phys.* **2014**, *141*, 184905.
[5] C. Corbisieri, P. Jousset, M. Roos, *J. Appl. Polym. Sci.* **2021**, *138*, e50662.
[6] A. A. Lacey, D. M. Price, M. Reading, in *Modulated Temperature Differential Scanning Calorimetry* (Eds: M. Reading, D. J. Hourston), Springer, Dordrecht **2006**, Ch. 1.
[7] E. Bittrich, F. Windrich, D. Martens, L. Bittrich, L. Häussler, K.-J. Eichhorn, *Polym. Test.* **2017**, *64*, 48.
[8] K. Dalnoki-Veress, J. A. Forrest, C. Murray, C. Gigault, J. R. Dutcher, *Phys. Rev. E* **2001**, *63*, 031801.

[9] J. A. Forrest, K. Dalnoki-Veress, *Adv. Colloid Interface Sci.* **2001**, *94*, 167.
[10] A. J. Kovacs, J. M. Hutchinson, J. J. Aklonis, in *The Structure of Non-Crystalline Materials* (Ed: P. H. Gaskell), Taylor & Francis, London **1977**.
[11] A. J. Kovacs, J. J. Aklonis, J. M. Hutchinson, A. R. Ramos, *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
[12] J. M. Hutchinson, A. J. Kovacs, *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1575.
[13] A. J. Kovacs, *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394.
[14] A. Lion, C. Mittermeier, M. Johlitz, *Continuum Mech. Thermodyn.* **2017**, *29*, 1061.
[15] I. Gutzow, D. Ilieva, F. Babalievski, V. Yamakov, *J. Chem. Phys.* **2000**, *112*, 10941.
[16] J. Möller, I. Gutzow, J. W. P. Schmelzer, *J. Chem. Phys.* **2006**, *125*, 094505.
[17] H. Baur, *Z. Naturforsch., A: Phys. Sci.* **1998**, *53*, 157.
[18] H. Baur, *Thermophysics of Polymers I: Theory*, Springer-Verlag, Berlin **1999**.
[19] H. Baur, B. Wunderlich, *J. Therm. Anal.* **1998**, *54*, 437.
[20] A. Lion, C. Liebl, S. Kolmeder, J. Peters, *J. Mech. Phys. Solids* **2010**, *58*, 1338.
[21] B. Kowalska, *Int. Polym. Sci. Technol.* **2002**, *29*, 76.
[22] J. Wang, C. Hopmann, M. Schmitz, T. Hohlweck, J. Wipperfürth, *Mater. Des.* **2019**, *183*, 108149.
[23] The variables v, T, and P denote the specific volume, temperature, and pressure, respectively. Θ_g corresponds to the temperature derivative of the specific volume in the vitreous state at temperatures sufficiently below the glass transition temperature T_g, i.e., $T \ll T_g$. In the equilibrium state, i.e., $T \gg T_g$, the temperature derivative of the specific volume reads $(\mathrm{d}v/\mathrm{d}T)_P^e = \Theta_g + \Delta\Theta$. θ_3 is a material-dependent parameter.
[24] H. Pastijn, in *The Logistic Map and the Route to Chaos* (Eds: M. Ausloos, M. Dirickx), Springer-Verlag, Berlin **2006**, Part I.
[25] A. D. Polyanin, V. F. Zaitsev, *Handbook of Ordinary Differential Equations*, CRC Press, Taylor & Francis Group, Boca Raton **2018**.
[26] The specific isobaric heat capacity in the vitreous state at temperatures sufficiently below the glass transition temperature is denoted by c_{Pg}. In the equilibrium state, the specific isobaric heat capacity reads $c_P^e = c_{Pg} + \Delta c_P$. μ_3 is a material-dependent parameter.
[27] B. D. Coleman, M. E. Gurtin, *J. Chem. Phys.* **1967**, *47*, 597.
[28] J.-L. Garden, H. Guillou, in *Encyclopedia of Glass Science, Technology, History, and Culture*, Vol. *1* (Eds: P. Richet, R. Conradt, A. Takada, J. Dyon), John Wiley & Sons, Hoboken, NJ **2021**, Ch. 3.2.
[29] N. L. Ellegaard, T. Christensen, P. V. Christiansen, N. B. Olsen, U. R. Pedersen, T. B. Schrøder, J. C. Dyre, *J. Chem. Phys.* **2007**, *126*, 074502.
[30] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Charles C Thomas Publisher, Illinois **1955**.
[31] S. R. de Groot, P. Mazur, *Non-Equilibrium Thermodynamics*, Dover Publications, New York **1984**.
[32] C. Truesdell, *Rational Thermodynamics*, 2nd ed., Springer-Verlag, New York **1984**.
[33] J. Meixner, *Arch. Rational Mech. Anal.* **1969**, *33*, 33.
[34] J. Meixner, *Z. Phys.* **1969**, *219*, 79.
[35] D. Jou, J. Casas-Vázquez, G. Lebon, *Extended Irreversible Thermodynamics*, 4th ed., Springer Science+Business Media, New York **2010**.
[36] G. A. Maugin, *The Thermomechanics of Nonlinear Irreversible Behaviors*, World Scientific Publishing, Singapore **1999**.
[37] B. D. Coleman, *Arch. Rational Mech. Anal.* **1964**, *17*, 1.
[38] M. E. Gurtin, *Arch. Rational Mech. Anal.* **1968**, *28*, 40.
[39] L. D. Landau, E. M. Lifschitz, *Lehrbuch der Theoretischen Physik*, Vol. V, Akademie-Verlag, Berlin **1987**.
[40] J. H. Gibbs, E. A. DiMarzio, *J. Chem. Phys.* **1958**, *28*, 373.
[41] W. Kauzmann, *Chem. Rev.* **1948**, *43*, 219.
[42] G. B. McKenna, S. L. Simon, *Macromolecules* **2017**, *50*, 6333.
[43] M. H. Cohen, G. S. Grest, *Phys. Rev. B* **1979**, *20*, 1077.
[44] H.-J. Oels, G. Rehage, *Macromolecules* **1977**, *10*, 1036.
[45] H. Breuer, G. Rehage, *Kolloid Z. Z. Polym.* **1967**, *216*, 159.
[46] R. O. Davies, G. O. Jones, *Adv. Phys.* **1953**, *2*, 370.
[47] M. Goldstein, in *Modern Aspects of the Vitreous State* (Ed: J. D. Mackenzie), Butterworth & Co. Publishers, London **1964**, Ch. 4.
[48] W. Fleming, *Functions of Several Variables*, 2nd ed., Springer-Verlag, New York **1977**.
[49] E. A. DiMarzio, *J. Appl. Phys.* **1974**, *45*, 4143.
[50] E. A. DiMarzio, *J. Chem. Phys.* **1977**, *67*, 2393.
[51] J. Meixner, *Kolloid-Zeitschrift* **1953**, *134*, 3.
[52] H.-W. Kammer, K. Schwabe, *Thermodynamik irreversibler Prozesse*, VCH Verlagsgesellschaft, Weinheim **1985**.
[53] I. L. Hopkins, *J. Polym. Sci.* **1958**, *28*, 631.
[54] O. S. Narayanaswamy, *J. Am. Ceram. Soc.* **1971**, *54*, 491.
[55] J. I. Berg, A. R. Cooper, *J. Chem. Phys.* **1978**, *68*, 4481.
[56] G. Adam, J. H. Gibbs, *J. Chem. Phys.* **1965**, *43*, 139.
[57] J. D. Ferry, *Viscoelastic Properties of Polymers*, John Wiley & Sons, New York **1961**.
[58] A. Q. Tool, *J. Am. Ceram. Soc.* **1946**, *29*, 240.
[59] P. B. Macedo, T. A. Litovitz, *J. Chem. Phys.* **1965**, *42*, 245.
[60] A. K. Doolittle, *J. Appl. Phys.* **1951**, *22*, 1471.
[61] R. P. White, J. E. G. Lipson, *Macromolecules* **2016**, *49*, 3987.
[62] M. L. Williams, R. F. Landel, J. D. Ferry, *J. Am. Chem. Soc.* **1955**, *77*, 3701.
[63] H. Vogel, *Phys. Z.* **1921**, *22*, 645.
[64] G. S. Fulcher, *J. Am. Ceram. Soc.* **1925**, *8*, 339.
[65] G. Tammann, W. Hesse, *Z. Anorg. Allg. Chem.* **1926**, *156*, 245.
[66] S. L. Simon, G. B. McKenna, in *Polymer Glasses* (Ed: C. B. Roth), CRC Press, Taylor & Francis Group, Boca Raton **2017**, Ch. 2.
[67] F. R. Schwarzl, A. J. Staverman, *J. Appl. Phys.* **1952**, *23*, 838.
[68] C. T. Moynihan, P. B. Macedo, C. J. Montrose, P. K. Gupta, M. A. DeBolt, J. F. Dill, B. E. Dom, P. W. Drake, A. J. Easteal, P. B. Elterman, R. P. Moeller, H. Sasabe, J. A. Wilder, *Ann. N. Y. Acad. Sci.* **1976**, *279*, 15.
[69] H. N. Ritland, *J. Am. Ceram. Soc.* **1956**, *39*, 403.
[70] G. M. Bartenev, *The Structure and Mechanical Properties of Inorganic Glasses*, Wolters-Noordhoff Publishing, Groningen **1970**.
[71] J. M. Hutchinson, A. J. Kovacs, in *The Structure of Non-Crystalline Materials* (Ed: P. H. Gaskell), Taylor & Francis, London **1977**.
[72] H. Baur, *Colloid & Polymer Sci.* **1978**, *256*, 833.
[73] M. Abramowitz, in *Handbook of Mathematical Functions* (Eds: M. Abramowitz, I. A. Stegun), Dover Publications, New York **1965**, Ch. 3.
[74] D. Zwillinger, V. Moll, I. S. Gradshteyn, I. M. Ryzhik, *Table of Integrals, Series, and Products*, 8th ed., Academic Press, Amsterdam **2014**.
[75] L. Papula, *Mathematische Formelsammlung*, 12th ed., Springer Vieweg, Wiesbaden **2017**.
[76] Clairaut's theorem states that the partial derivatives of a generic function $f(x, y, z)$, under the hypothesis of continuity of the partial derivatives, are equal according to $\partial^2 f/\partial x\partial y = \partial^2 f/\partial y\partial x$, $\partial^2 f/\partial x\partial z = \partial^2 f/\partial z\partial x$, and $\partial^2 f/\partial y\partial z = \partial^2 f/\partial z\partial y$.[48, 75, 77]
[77] L. F. Richardson, *Advanced Calculus*, John Wiley & Sons, Hoboken, NJ **2008**.
[78] I. A. Stegun, in *Handbook of Mathematical Functions* (Eds: M. Abramowitz, I. A. Stegun), Dover Publications, New York **1965**, Ch. 27.
[79] L. A. Wood, *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 703.
[80] G. Rehage, H. Breuer, *J. Polym. Sci., Part C: Polym. Symp.* **1967**, *16*, 2299.
[81] G. Rehage, W. Borchard, in *The Physics of Glassy Polymers* (Ed: R. N. Haward), Applied Science Publishers, London **1973**, Ch. 1.
[82] J. W. P. Schmelzer, T. V. Tropin, *Thermochim. Acta* **2019**, *677*, 42.

