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Freezing-in and production of entropy in vitrification

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Following the classical concepts developed by Simon [Z. Anorg. Allg. Chem. **203**, 219 (1931)], vitrification in the cooling of glass-forming melts is commonly interpreted as the transformation of a thermodynamically (meta)stable equilibrium system into a frozen-in, thermodynamically nonequilibrium system, the glass. Hereby it is assumed that the transformation takes place at some well-defined sharp temperature, the glass transition temperature T_g . However, a more detailed experimental and theoretical analysis shows that the transition to a glass proceeds in a broader temperature range, where the characteristic times of change of temperature, $\tau_T = -(T/\dot{T})$, and relaxation times, τ , of the system to the respective equilibrium states are of similar order of magnitude. In this transition interval, the interplay of relaxation and change of external control parameters determines the value of the structural order parameters. In addition, irreversible processes take place in the transition interval, resulting both in an entropy freezing-in as well as in an irreversible increase of entropy and, as a result, in significant changes of all other thermodynamic parameters of the vitrifying systems. The effect of entropy production on glass transition and on the properties of glasses is analyzed here for the first time. In this analysis, the structural order-parameter concept as developed by de Donder and van Rysselberghe [*Thermodynamic Theory of Affinity* (Stanford University Press, Stanford, 1936)] and Prigogine and Defay [*Chemical Thermodynamics* (Longmans, London, 1954)] is employed. In the framework of this approach we obtain general expressions for the thermodynamic properties of vitrifying systems such as heat capacity, enthalpy, entropy, and Gibbs' free energy, and for the entropy production. As one of the general conclusions we show that entropy production has a single maximum upon cooling and two maxima upon heating in the glass transition interval. The theoretical concepts developed allow us to explain in addition to the thermodynamic parameters also specific features of the kinetic parameters of glass-forming melts such as the viscosity. Experimental results are presented which confirm the theoretical conclusions. Further experiments are suggested, allowing one to test several additional predictions of the theory. © 2006 American Institute of Physics. [DOI: [10.1063/1.2346673](https://doi.org/10.1063/1.2346673)]

I. INTRODUCTION

Following the classical concepts developed by Simon,^{1,2} vitrification of a glass-forming melt in cooling is commonly interpreted as a freezing-in process. Hereby it is assumed that above a given temperature, T_g , the glass-forming melt is able to reach at any moment of time the actual stable or metastable equilibrium state, i.e., processes of relaxation of the system to these states are expected to proceed rapidly when compared with changes of the external control parameter (here temperature). Below the glass transition temperature, the system is assumed to be in a completely frozen-in, non-equilibrium state. Here slow relaxation processes may occur, in general, as well. However, due to very small kinetic coefficients the system cannot reach the respective equilibrium states in the time scales of the experimental investigations. As a result, the system is characterized by excess frozen-in

values of entropy, enthalpy, Gibbs' free energy, etc., as compared with the respective metastable or stable equilibrium states.²

However, a detailed experimental and theoretical investigation of vitrification shows^{3,4} that in cooling a liquid, the transition from the undercooled metastable equilibrium melt to a frozen-in nonequilibrium state, the glass, does actually proceed in a certain temperature range. We denote the upper and lower boundaries of this temperature range as T_g^+ and T_g^- , respectively. Inside this temperature range ($T_g^- < T < T_g^+$), the characteristic times, $\tau_T = -(T/\dot{T})$, of change of the externally governed parameters (here temperature) are comparable in magnitude with the characteristic times, τ , of relaxation to the respective temporary stable or metastable equilibrium states. Indeed, the definition of the characteristic time of change of temperature implies that the change of temperature in a time interval dt is given by the relation $dT/dt = -(T/\tau_T)$. Similarly (as will be discussed in detail below), relaxation processes of glass-forming melts to the respective

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equilibrium states are governed by equations of the type $d\xi = -(\xi - \xi_e)/\tau$, where ξ is here some characteristic parameter of the glass-forming melt and ξ_e is its value in the stable or metastable equilibrium state of the system.

For $\tau_T \gg \tau$, the glass-forming system remains in the course of the cooling process in a state of thermodynamic equilibrium; in the opposite case, $\tau_T \ll \tau$, the glass-forming melt is practically frozen-in. Consequently, in the temperature range, defined by $\tau_T \approx \tau$, the system goes over from a metastable equilibrium state to a frozen-in nonequilibrium state, the glass. The vitrification interval can be defined—according to these considerations—generally via the relation $\tau_T \approx \tau$ or, employing the definition of the characteristic time of change of the control parameter, by

$$\left(\frac{1}{T} \frac{dT}{dt}\right) \tau \approx \text{const} \quad \text{at} \quad T \approx T_g, \quad (1)$$

where the constant is of the order of unity. The validity of relations equivalent to Eq. (1) has been established first experimentally; they are known as the Frenkel-Kobeko rule (see Ref. 2). The theoretical analysis performed here shows that the validity of Eq. (1) is a consequence of the very deep nature of vitrification processes (see Refs. 2–4), they have to be fulfilled consequently for any freezing-in process independent of the rate of change of the external control parameters and the nature of the vitrifying system. For this reason, in the vitrification interval processes of change of the external control parameters are always accompanied by irreversible processes of relaxation of the system to the respective equilibrium states. These irreversible processes do occur in the system in cooling as well as in heating, resulting—according to the basic laws of thermodynamics—in a production of entropy. The continuity in the transition from the metastable equilibrium state to the frozen-in nonequilibrium state, the glass, and the resulting entropy production in this temperature range ($T_g^- \leq T \leq T_g^+$) is, consequently, a general feature of any glass transition. Variations of the rate of change of the control parameters may shift [according to Eq. (1)] the position of the vitrification interval, but do not affect the existence of the effect itself. Again, the shift of the glass transition temperature in dependence on cooling rate has been established first experimentally; it is well-known as the Bartenev-Ritland equation.² It can be shown that the Bartenev-Ritland equation is also a direct consequence of Eq. (1) (see Refs. 3 and 4).

The interpretation of vitrification as proceeding in a finite temperature interval and the resulting necessarily account of entropy production terms have, as will be shown in the present analysis, significant effects and are of principal importance for the correct understanding of a variety of thermodynamic and kinetic characteristics of glass-forming melts also beyond the circle of problems discussed here (see Ref. 5). The effect of entropy production in vitrification has not been accounted for up to now in the analysis of the thermodynamic properties of glass-forming systems in heating and cooling or in any other possible mechanisms of vitrification, e.g., due to pressure changes. It is the aim of the present investigation to fill this gap. Hereby we employ the method developed by de Donder and van Rysselberghe⁶ and

Prigogine and Defay⁷ characterizing the system under consideration by a set of structural order parameters introduced into the description in addition to the conventional thermodynamic state parameters.

The paper is structured as follows: In Sec. II, we give a summary—following de Donder and van Rysselberghe⁶ and Prigogine and Defay⁷—of the basic thermodynamic equations utilized in the present analysis. In order to employ these general dependences, basic general thermodynamic and kinetic properties of glass-forming systems have to be known. In the present analysis, we use for these purposes a simple but qualitatively accurate lattice-hole model of glass-forming systems. The essential features of this model and the basic equations employed for the description of relaxation of glass-forming melts are summarized in Sec. III. In Sec. IV, the general thermodynamic equations derived are applied to the derivation of the expressions for the change of entropy, enthalpy, and a variety of other thermodynamic functions in cyclic heating-cooling processes, performed (as the simplest realization) with constant heating and cooling rates. We assume hereby that the cooling process starts at a sufficiently high temperature above T_g at a well-defined stable or metastable equilibrium state. The process is then terminated at a sufficiently low temperature, when the system is completely frozen-in for the experimental time scales considered. Then the system is reheated at the same constant rate until the initial metastable or stable state is reestablished (i.e., it is supposed that the characteristic relaxation times at this state are considerably smaller as compared with the characteristic times of variation of the external parameter). The consequences are discussed in detail, and a first comparison with experimental data is given. Further experimental analyses are suggested, allowing one to test specific features of the theory outlined. The relevance of the method of description of vitrification employed and of the results obtained with respect to the understanding of the behavior of the kinetic parameters of glass-forming melts such as viscosity is briefly analyzed in Sec. V. A summary of the results and their implications and the discussion of future possible developments (Sec. VI) complete the paper.

II. BASIC THERMODYNAMIC EQUATIONS

A. General dependences

In treating vitrification processes, we have to consider systems in thermodynamic nonequilibrium states. In such states, the change of the entropy S in any process consists, in general, of two terms,⁷

$$dS = d_e S + d_i S, \quad d_e S = \frac{dQ}{T}, \quad d_i S \geq 0. \quad (2)$$

Here $d_i S$ describes changes of the entropy connected with irreversible processes taking place in the system under consideration, while the term $d_e S$ describes changes of the entropy connected with an exchange of energy in the form of heat, dQ , with surrounding systems (denoted further as heat bath). T here is denoted originally as the temperature of the heat bath (assumed to be in an internal thermal equilibrium) exchanging energy in form of heat with the system, where

the processes under consideration take place. In our analysis, we assume that the heat bath and the system analyzed are always sustained at states near internal thermal equilibrium and that, with respect to temperature, a state near equilibrium between heat bath and system is established at any time. In such cases, the temperature of the system under consideration and the temperature of the heat bath are equal. In other words, we do not consider here changes of the entropy due to the transfer of energy in form of heat between systems sustained at different temperatures.

Following de Donder and van Rysselberghe⁶ and Prigogine and Defay,⁷ we can describe processes of relaxation of glass-forming melts to the respective metastable equilibrium state by the introduction of additional appropriately chosen structural order parameters, ξ_i . Here we assume that the system can be described with a sufficient degree of accuracy by only one such additional order parameter, ξ . Such an assumption is always suitable when basically qualitative consequences of theoretical concepts are considered. If desired the derivations given below can be easily extended to more complex situations by taking into account, as it is done sometimes in the literature,^{8–10} the existence of several independent order parameters. However, in the vicinity of the glass transition temperature, where the effects discussed are of major significance, the free volume of the glass-forming melt decreases dramatically with decreasing temperature. As a result, possible alternative structural parameters may become dependent on free volume and cannot be considered then anymore as independent (see Ref. 8–11). In an accompanying paper, it has been shown by two of the present authors⁵ that the known experimental data on the so-called Prigogine-Defay ratio in vitrification can be interpreted theoretically in terms of the theoretical approach developed here by employing only one structural order parameter. This result is considered as one direct experimental proof of the validity of our approach and confirms us, moreover, in our belief that the restriction to one structural order parameter may give not only a qualitatively but even a quantitatively correct description of thermodynamic properties of glass-forming melts in vitrification. Anyway, the theoretical method developed here can be extended easily to the case that several independent structural order parameters have to be utilized for the description of the system under consideration.

Assuming that a single structural order parameter is sufficient for the description of the degree of deviation of the glass-forming melt from the respective stable or metastable equilibrium state, the combined first and second laws of thermodynamics can be written then in the form^{6,7}

$$dU = TdS - pdV - Ad\xi. \quad (3)$$

Here U is the internal energy and V the volume of the system, p the external pressure, and A the affinity of the process of structural relaxation considered. Since the number of particles of the different components remains constant (i.e., we consider closed systems), terms describing their possible changes do not occur in Eq. (3) in the applications analyzed. Since for any irreversible processes taking place at constant entropy and volume, the internal energy can only decrease,^{12,13} the relation $Ad\xi \geq 0$ has to be fulfilled.

A combination of Eqs. (2) and (3) yields

$$dU = Td_eS + Td_iS - pdV - Ad\xi. \quad (4)$$

Alternatively, for any (reversible or irreversible) process of a thermodynamic system, we have according to the first law of thermodynamics^{12,13}

$$dU = dQ - pdV = Td_eS - pdV. \quad (5)$$

Consequently, the relations

$$Td_iS = Ad\xi \text{ or } d_iS = \left(\frac{A}{T}\right)d\xi \quad (6)$$

have to be fulfilled, in general. It follows from the latter equation that equilibrium states are characterized by $A=0$. Only for such states, the production term of the entropy, d_iS , connected with possible irreversible processes in the system, is equal to zero. Moreover, since the changes of entropy and order parameter take place in the same time interval, dt , we can rewrite Eq. (6) also as

$$T \frac{d_iS}{dt} = A \frac{d\xi}{dt} \text{ or } \frac{d_iS}{dt} = \left(\frac{A}{T}\right) \frac{d\xi}{dt}. \quad (7)$$

In this way, we rederived the basic relationship connecting variations of entropy and structural order parameter.⁷ However, in order to employ this relation, we have to express also the affinity A via the basic thermodynamic functions.

Employing pressure and temperature as the thermodynamic state parameters and assuming, in addition to thermal equilibrium, that the conditions of mechanical equilibrium are fulfilled (equality of pressure of the heat bath and of the system under consideration), the characteristic thermodynamic potential is the Gibbs free energy G defined generally via

$$G = U - TS + pV. \quad (8)$$

Equation (3) yields

$$dG = -SdT + Vdp - Ad\xi, \quad (9)$$

and the required second necessary relation for the affinity can be obtained in the form

$$A = - \left(\frac{\partial G}{\partial \xi} \right)_{p,T}. \quad (10)$$

At constant pressure and temperature, the thermodynamic equilibrium state is characterized by a minimum of Gibbs' free energy G . Let us denote further by ξ_e the value of the order parameter ξ in this equilibrium state. Since in thermodynamic equilibrium, the state of the considered closed system is determined by two independent variables, the equilibrium value of the structural order parameter can be represented as an unambiguous function of pressure and temperature, i.e.,

$$\xi_e = \xi_e(p, T). \quad (11)$$

A truncated Taylor expansion of the partial derivative of Gibbs' free energy with respect to the order parameter ξ in the vicinity of the respective equilibrium state, $\xi = \xi_e$, results in

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \cong G_e^{(2)}(p,T,\xi_e)(\xi - \xi_e), \quad (12)$$

$$G_e^{(2)}(p,T,\xi_e) = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T,\xi=\xi_e}.$$

The first term in the expansion, $(\partial G/\partial \xi)_{p,T,\xi=\xi_e}$, vanishes since Gibbs' free energy has a minimum at equilibrium ($\xi = \xi_e$). For the affinity A we obtain from Eqs. (10) and (12)

$$A = -G_e^{(2)}(\xi - \xi_e), \quad (13)$$

$$G_e^{(2)} = G_e^{(2)}(p,T,\xi_e) = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T,\xi=\xi_e} > 0.$$

The parameter $G_e^{(2)}$ has to be positive, since the equilibrium state is characterized by a minimum of Gibbs' free energy.

B. Application of basic ideas of the thermodynamics of irreversible processes

Thermodynamics of irreversible processes^{14,15} states that the fluxes (here the change of ξ) are functions of the thermodynamic driving forces (here the affinity A). In this way, we may write

$$\frac{d\xi}{dt} = Lf(X), \quad X = \frac{A}{RT}, \quad (14)$$

going over from the affinity A to the dimensionless thermodynamic driving force X . Here R is the universal gas constant and L a kinetic coefficient, depending on pressure and temperature but not on the order parameter ξ . The function $f(X)$ is not known, in general. It can be specified by introducing, in the framework of statistical models, certain assumptions concerning the system under consideration or by employing experimental results.^{2,3,14} We will return to different methods of specification of this function below. However, first we study several general consequences connected with the definition of this function.

In thermodynamic equilibrium, the relations

$$A = 0, \quad \xi = \xi_e, \quad \frac{d\xi}{dt} = 0 \quad (15)$$

hold and, consequently, we have to demand $f(X=0)=0$. Moreover, employing the methods of the linear thermodynamics of irreversible processes (applicable for sufficiently small deviations from equilibrium), the evolution equations are commonly written in the form

$$\frac{d\xi}{dt} = -L \frac{\partial}{\partial \xi} \left(\frac{G}{RT} \right). \quad (16)$$

Equations (10), (14), and (16) yield a second condition the function $f(X)$ has to obey, i.e., $(\partial f(X)/\partial X)|_{X=0}=1$.

By a Taylor expansion of the function $f(X)$ in the vicinity of the thermodynamic equilibrium state ($X=0$) we obtain [with $f(0)=0$ and $(\partial f(X)/\partial X)|_{X=0}=1$] the relation

$$f(X) = X + \frac{1}{2}f''(0)X^2 + \dots, \quad f''(0) = \left. \frac{d^2 f(X)}{dX^2} \right|_{X=0}. \quad (17)$$

Retaining in the Taylor expansion of the function $f(X)$ terms of up to the second order in X , only, Eq. (14) can be written in the form

$$\frac{d\xi}{dt} \cong -\frac{LG_e^{(2)}}{RT} \left(1 - \frac{f''(0)G_e^{(2)}}{2RT}(\xi - \xi_e) \right) (\xi - \xi_e). \quad (18)$$

Here, in addition, Eq. (13) has been employed.

Introducing a characteristic time scale of the relaxation processes, τ , via

$$\frac{1}{\tau} = \frac{LG_e^{(2)}}{RT} \left(1 - \frac{f''(0)G_e^{(2)}}{2RT}(\xi - \xi_e) \right), \quad (19)$$

Eq. (18) yields

$$\frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi_e). \quad (20)$$

For very small deviations from equilibrium ($\xi \cong \xi_e$), quadratic terms in the difference $(\xi - \xi_e)$ vanish and we obtain

$$\frac{d\xi}{dt} = -\frac{1}{\tau_e}(\xi - \xi_e), \quad (21)$$

with a characteristic relaxation time, $\tau_e = (RT/LG_e^{(2)})$, depending on pressure and temperature but not on the order parameter ξ . Retaining terms of second order in the difference $(\xi - \xi_e)$, we can write, consequently,

$$\begin{aligned} \tau(p,T,\xi) &= \tau_e \left(1 - \frac{f''(0)G_e^{(2)}}{2RT}(\xi - \xi_e) \right)^{-1} \\ &\cong \tau_e \left(1 + \frac{f''(0)G_e^{(2)}}{2RT}(\xi - \xi_e) \right). \end{aligned} \quad (22)$$

Not only did we specify in this way the relaxation law but we also introduced a dependence of the characteristic relaxation time on the value of the order parameter ξ . Since the parameters $f''(0)$ and $G_e^{(2)}$ depend on the properties of the system in the respective equilibrium state, exclusively, it follows from Eq. (22) that the relaxation times are different, in general, in dependence on whether the inequalities $(\xi - \xi_e) > 0$ or $(\xi - \xi_e) < 0$ hold, i.e., from which side the system tends at isothermal conditions to the respective equilibrium state.

The kinetic equation, formulated with Eqs. (20) and (22), can be denoted as a quasilinear relaxation law. It is linear with respect to the difference, $(\xi - \xi_e)$, but with a characteristic relaxation time τ depending also on this difference. Note that this quasilinear character of the relaxation law can be obtained also in the general case if we do not expand the function $f(X)$ into a Taylor series. Equations (14) and (20) lead, employing further the expression for τ_e derived, to the conclusion that generally the quasi-linear relaxation law holds where the relaxation time can be expressed—in the most general form—as

$$\frac{1}{\tau} = \frac{1}{\tau_e} \left\{ \frac{RTf(X)}{G_e^{(2)}(\xi - \xi_e)} \right\}. \quad (23)$$

Employing the Taylor expansion of the function $f(X)$ [see Eq. (17)], Eq. (19) is reestablished from this general relation as a special case, again.

Equations (7), (13), and (20) yield the following expression for the entropy production in the system due to irreversible relaxation:

$$\frac{d_i S}{dt} = \frac{G_e^{(2)}}{T\tau} (\xi - \xi_e)^2. \quad (24)$$

As it should be the case, the entropy production term is always a positive quantity independent of the sign of the deviation of the order parameter from its equilibrium value, $(\xi - \xi_e)$, since the relaxation time τ is a positive quantity. This condition has to be fulfilled, consequently, in any model considerations concerning the function $f(X)$ in order to lead to physically meaningful results.

In establishing the basic equations of the theory, we employed one as evident from the derivations—exclusively basic laws of classical thermodynamics and thermodynamics of irreversible processes. The theoretical method is consequently model independent and generally applicable. An approximation is employed only once (a truncated Taylor expansion is performed), leading to the expression for the affinity, Eq. (13). In order to derive the principal consequences of the theory outlined, in the next section thermodynamic and kinetic properties of glass-forming melts are specified in more detail. In particular, a lattice-hole model of glass-forming melts is introduced, allowing us to describe the most essential qualitative features of any vitrification processes. For a wide class of glass-forming melts, it is even able to describe the behavior quantitatively. In the course of specification of this model, the definition of the order parameter we used in our computations is specified. As will be shown, with such choice all the above given relations are fulfilled in the vicinity of ξ_e and even beyond. However, for particular applications other choices of the structural order parameters may be useful or desirable and can be employed since the above relations are exclusively consequences from very basic and general thermodynamic laws valid for any appropriate choice of the order parameter. This freedom ensures that the equations cited above hold for any particular realizations of glass transitions, since these equations are perfectly general. A more detailed discussion of general mathematical aspects of possible appropriate choices of structural order parameters and their transformations will be given in a forthcoming paper.¹⁶

III. PROPERTIES OF GLASS-FORMING MELTS: BASIC MODEL ASSUMPTIONS

A. Kinetics of relaxation

A large amount of experimental data shows that the characteristic relaxation times of glass-forming melts in stable or metastable equilibrium states can be generally expressed in the form²

$$\tau_e = \tau_0 \exp\left(\frac{U_a(p, T)}{RT}\right), \quad \tau_0 = \frac{k_B T}{h}, \quad (25)$$

where the activation energy U_a of the relaxation processes obeys the inequality

$$\frac{dU_a(p, T)}{dT} \leq 0. \quad (26)$$

As a typical example, we will employ here the Vogel-Fulcher-Tammann equation,² where the activation energy can be written as

$$U_a(p, T) = U_a^* \left(\frac{T}{T - T_0} \right). \quad (27)$$

Here U_a^* and T_0 are empirical constants specific for the substance considered. We identify the parameter T_0 with Kauzmann's temperature (see Ref. 2) and set it equal in the following model computations to $T_0 = T_m/2$, where T_m is the melting or liquidus temperature of the liquid. At the glass transition temperature T_g , the activation energy U_a is of the order $U_a(T_g)/RT_g \approx 30$. With $T_g/T_m \approx 2/3$, we obtain as an estimate $U_a^*/RT_g = 7.5$. The preexponential term, τ_0 , in Eq. (25) is determined basically by the frequency of molecular oscillations. It is practically not affected by deviations of the system from the respective equilibrium state. For an estimate of its value, we employ here the relation $\tau_0 = (k_B T/h)$, where h is Planck's constant.

In order to account for the effect of deviations of the system from equilibrium on its relaxation behavior, the activation energy U_a has to be considered as a function not only of pressure and temperature but also of the structural order parameter ξ . By means of a Taylor expansion of the thus introduced function $U_a(T, p, \xi)$ in the vicinity of the respective equilibrium state, $\xi = \xi_e$, we obtain in a linear approximation with respect to the difference $(\xi - \xi_e)$

$$U_a(p, T, \xi) = U_a(p, T) + \left(\frac{\partial U_a}{\partial \xi} \right) \bigg|_{p, T, \xi = \xi_e} (\xi - \xi_e). \quad (28)$$

Instead of Eq. (25), we may write then the following dependence for the relaxation time of a glass-forming melt in a thermodynamically nonequilibrium state:

$$\begin{aligned} \tau &= \tau_0 \exp\left(\frac{U_a(p, T, \xi)}{RT}\right) \\ &= \tau_e \exp\left(\frac{1}{RT} \left(\frac{\partial U_a}{\partial \xi} \right) \bigg|_{p, T, \xi = \xi_e} (\xi - \xi_e)\right). \end{aligned} \quad (29)$$

A Taylor expansion of the exponential term in Eq. (29) results in

$$\tau \approx \tau_e \left(1 + \frac{1}{RT} \left(\frac{\partial U_a}{\partial \xi} \right) \bigg|_{p, T, \xi = \xi_e} (\xi - \xi_e) \right). \quad (30)$$

A comparison of this approximation with the result derived here earlier in an alternative way and given by Eq. (22) shows that they are identical when the condition

$$\frac{f''(0)G_e^{(2)}}{2} = \frac{1}{RT} \left(\frac{\partial U_a}{\partial \xi} \right) \bigg|_{p,T,\xi=\xi_e} \quad (31)$$

holds. In this way, we have found a third requirement the function $f(X)$ has to fulfill in order to describe adequately relaxation processes in glass-forming melts.

In addition to the discussed coincidence in the expressions for the relaxation times, derived here in two different ways, Eqs. (28) and (29) can be given additional support based on well-known ideas of the theory of absolute reaction rates¹⁷ and Prigogine's analysis of the probability of fluctuations in thermodynamic nonequilibrium systems.¹⁸ A detailed analysis of the respective concepts in application to the problems considered here is given in Refs. 3 and 4.

B. Thermodynamic properties

For the specification of the thermodynamic properties of glass-forming melts, we employ here relations derived from a simple lattice-hole model of liquids discussed in detail in Ref. 2. The structural order parameter is connected in the framework of this model with the free volume of the liquid and defined via the number of unoccupied sites (or holes) N_0 per mole of the liquid, each of them having a volume $v_0(p, T)$ identical to the volume of a structural unit of the liquid at the same values of pressure and temperature. According to this model, the molar volume of the liquid is determined as^{2,5}

$$V(p, T, \xi) \cong N_A v_0(p, T)(1 + \xi), \quad \xi = \frac{N_0}{N_A + N_0} \cong \frac{N_0}{N_A}. \quad (32)$$

Here N_A is the Avogadro's number.

The thermodynamic functions of the system are described in the framework of this model by the sum of contributions resulting from the thermal motion of the molecules of the liquid and, in addition, from the configurational contributions described by the structural order parameter ξ . The configurational contribution to the volume is given, consequently, by

$$V_\xi \cong N_A v_0(p, T) \xi. \quad (33)$$

The configurational contribution to the enthalpy H_ξ of one mole of the liquid is described in the framework of this lattice-hole model via the molar heat of evaporation $\Delta H_{ev}(T_m)$ of the liquid at the melting temperature as

$$H_\xi = \chi_1 \Delta H_{ev}(T_m) \xi. \quad (34)$$

The parameter χ_1 will be determined later. Experimental data show that the molar heat of evaporation can be expressed for a wide class of liquids in accordance with Trouton's rule (see Fig. 1) as

$$\Delta H_{ev}(T_m) \cong \chi_2 RT_m \quad \text{with } \chi_2 = 20. \quad (35)$$

The configurational part of the entropy per mole is described in this model via the conventional mixing term

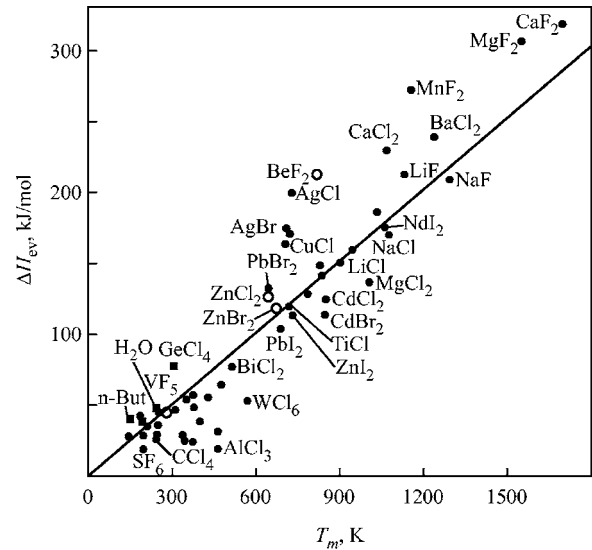


FIG. 1. Molar heat of evaporation ΔH_{ev} in dependence on melting temperature T_m for different halide and oxide substances with very different compositions (the circles refer to typical glass formers, while the full dots to substances not vitrified as yet). The black squares represent data for simple nonhalide glass formers (Ref. 19). The straight line is given as a confirmation of Eq. (35) employed in the analysis.

$$S_\xi = -R \left(\ln(1 - \xi) + \frac{\xi}{1 - \xi} \ln \xi \right). \quad (36)$$

With $H = U + pV$, we obtain for the configurational contribution to the internal energy the relation

$$U_\xi = [\chi_1 \Delta H_{ev}(T_m) - p v_0(p, T)] \xi. \quad (37)$$

Finally, employing the definition of Gibbs' free energy, Eq. (8), we arrive at

$$G_\xi = \chi_1 \Delta H_{ev}(T_m) \xi + RT \left(\ln(1 - \xi) + \frac{\xi}{1 - \xi} \ln \xi \right). \quad (38)$$

The equilibrium value of the structural order parameter, $\xi = \xi_e$, is determined via the relation $(\partial G / \partial \xi)_{p,T} = (\partial G_\xi / \partial \xi)_{p,T} = 0$. With Eqs. (35) and (38), we obtain the following result:

$$\frac{(1 - \xi_e)^2}{\ln \xi_e} = -\frac{1}{\chi} \left(\frac{T}{T_m} \right), \quad (39)$$

where $\chi = \chi_1 \chi_2$. Knowing the value of χ_2 [see Eq. (35)], we determine the value of the parameter χ_1 demanding that at $T = T_m$ the value of ξ_e should be approximately equal to 0.05 (corresponding to experimentally observed density differences between liquid and crystal at the melting temperature T_m). In the computations performed here we set $\chi_2 = 20$ and $\chi_1 = 0.166$, resulting in $\chi = 3.32$.

As it should be the case, in the vicinity of the state of configurational equilibrium, we obtain from Eq. (38) after performing a truncated Taylor expansion the result

$$G_\xi(p, T, \xi) \cong G_\xi(p, T, \xi_e) + \frac{1}{2} \left(\frac{\partial^2 G_\xi}{\partial \xi^2} \right) \bigg|_{p,T,\xi=\xi_e} (\xi - \xi_e)^2. \quad (40)$$

The value of $G_e^{(2)} = (\partial^2 G_\xi / \partial \xi^2) \big|_{\xi=\xi_e}$ at equilibrium and, consequently, the affinity of the process of structural relaxation

[see Eq. (13)] can now be easily calculated based on Eqs. (38) and (39). For small values of ξ , we get as an estimate $G_e^{(2)} \cong (RT/\xi_e)$. Moreover, knowing the dependence of the order parameter on temperature [see Eq. (39)], one can establish the deviations of all thermodynamic functions discussed above from the respective equilibrium values. For this reason, the determination of the function $\xi = \xi(T)$ is of basic importance for the understanding of the behavior of the thermodynamic properties of vitrifying melts. The method of determination of this dependence is discussed in the next section.

IV. KINETICS OF NONISOTHERMAL RELAXATION AS A MODEL OF THE GLASS TRANSITION: CHANGE OF THE THERMODYNAMIC FUNCTIONS IN CYCLIC COOLING-HEATING PROCESSES

A. Description of the cyclic processes under consideration

In the further analyses, we consider cyclic processes of the following type: At constant pressure, we cool the system with a constant rate,

$$q = \frac{dT}{dt} = \text{const.} \quad (41)$$

Since, according to Eq. (41), dT and dt are linearly dependent, we can always go over from a differentiation or integration with respect to time to the respective procedures with respect to temperature ($dT=qdt$) and vice versa ($dt=dT/q$) with different signs of the parameter q ($q < 0$ for cooling and $q > 0$ for heating processes). Equation (20) then takes the form^{3,4}

$$\frac{d\xi}{dT} = -\frac{1}{q\tau}(\xi - \xi_e). \quad (42)$$

Equation (42) was used in 1956 [without detailed derivation, and assuming $\tau = \tau_e$ with $U_a(p, T) = U_0 = \text{const}$; see Eq. (25)], in application to vitrification by Vol'kenstein and Ptizyn²⁰ and even earlier (in 1934) with the same restrictions by Bragg and Williams²¹ in the analysis of formation of metastable alloys. For this reason, we denote Eq. (42) as the Bragg-Williams equation (see Refs. 3 and 4).

We start the cyclic process at some well-defined stable or metastable equilibrium state. We denote the temperature of this equilibrium state of the liquid by T_l . In the cooling process, the internal order parameter ξ cannot follow, in general, the change of temperature of the system. Consequently, it can be represented as a function not only of pressure and temperature but also of the rate of change q of temperature, i.e.,

$$\xi = \xi(p, T, q). \quad (43)$$

From a mathematical point of view, Eq. (43) is a direct consequence of the differential equation, Eq. (42). Since the derivative ($d\xi/dT$) depends on the heating and cooling rates q , the solution has to depend on these parameters as well.

Reaching temperatures sufficiently below the temperature of vitrification, T_g , the relaxation time becomes extremely large [see Eq. (25)], and the value of ξ becomes

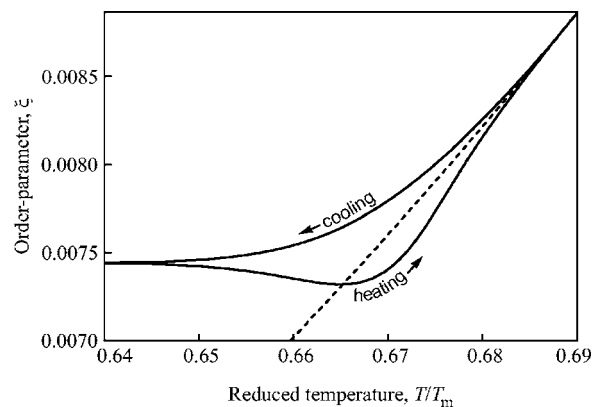


FIG. 2. Dependence of the structural order parameter, $\xi = \xi(p, T, q)$ [or $\xi = \xi(\theta)$ with $\theta = T/T_m$], in a cyclic cooling-heating process (full curve). The arrows indicate the direction of change of temperature. By a dashed curve, the equilibrium curve $\xi_e = \xi_e(\theta)$ is shown. In undercooling a liquid, the order parameter cannot follow, in general, the change of the external parameter and deviates from the equilibrium value ξ_e , resulting in $\xi > \xi_e$. Such kind of behavior is found in the vicinity of the glass transition temperature when the time scales of change of the external parameter become comparable with the characteristic relaxation times of the system. In heating, ξ decreases first until, after intersection with the equilibrium curve, it rapidly approaches this equilibrium curve from below due to the exponential decrease of the relaxation times with increasing temperature. For the computations, we used here $T_m = 750$ K, $T_0 = T_m/2$, $T_g \cong (2/3)T_m$, $\chi_1 = 0.166$, $\chi_2 = 20$, $\chi = 3.32$, and the relations $U_a(T_g)/RT_g = 30$ and $U_a^*/RT_g = 7.5$. The values of the other parameters employed are given in the text.

frozen-in, i.e., it practically does not change anymore in the time scales of the experiment. At and below this temperature, which we denote as T_s , the glass behaves as a solid body. Reversing now the process (again the pressure being fixed) and heating up the system with the same heating rate (with respect to its absolute value), we arrive after some time at the initial state, again. We assume in this way that the initial state is sufficiently near the melting temperature so that the characteristic times of relaxation become small as compared with the characteristic times of heating of the sample. In the course of the heating process, the structural order parameter is an unambiguous function of the heating rate, again, similar to the case of cooling. Note, however, that the function will be different for heating and cooling. Mathematically, this difference is expressed in Eq. (43) by the differences in the sign of the rate of change of temperature, being negative for cooling ($q < 0$) and positive for heating ($q > 0$) processes.

B. Structural order parameter and entropy production

As mentioned in the previous section, the knowledge of the temperature dependence of the structural order parameter is of essential significance in order to determine the properties of glass-forming melts in vitrification and in the process of reheating of the glass. For this reason, we start the analysis of the behavior of thermodynamic functions in vitrification with the discussion of this thermodynamic parameter.

An example for the change of the structural order parameter ξ in dependence on temperature, obtained via the numerical integration of Eq. (42), is shown in Fig. 2. We start the process at $T_l = T_m$ and cool the system down to $T_s = T_0 = T_m/2$. For convenience, we introduce the reduced temperature $\theta = (T/T_m)$. Equation (42) yields then

$$\frac{d\xi}{d\theta} = -\frac{1}{q_{\theta}\tau}(\xi - \xi_e), \quad q_{\theta} = \frac{d\theta}{dt}, \quad \theta = \frac{T}{T_m}. \quad (44)$$

Consequently, in terms of the reduced temperature θ , the considered temperature range is $0.5 \leq \theta \leq 1$.

We express the relaxation time τ [cf. Eq. (29)] for the computations in the form

$$\tau = \left(\frac{k_B T_m}{h} \right) \theta \exp \left(\frac{U_a^*}{RT_m(\theta - \theta_0)} \right) \exp \left(\frac{\chi_1 \Delta H_{ev}(\xi - \xi_e)}{RT_m \theta} \right). \quad (45)$$

In this way, it is supposed for the computations that the configurational part of the activation energy behaves similar to the configurational part of the internal energy of the glass-forming melt. Independent of this particular assumption, the relaxation time τ increases exponentially with decreasing temperature. It follows that the characteristic times of relaxation of the system to the respective equilibrium states become, in the course of cooling, first comparable to (in the vitrification interval) and then considerably larger than (below it) the characteristic times of change of the external parameters, here the temperature. As a result, the order parameter ξ retains higher values as compared with its equilibrium value ξ_e at the vitrification interval and below it.

The values of the characteristic temperatures T_g^+ (upper boundary of the vitrification interval), T_g (glass transition temperature), and T_g^- (lower boundary of the vitrification interval) depend on the cooling rate. The absolute value of the cooling rate is determined in the present computations via the condition [cf. Eq. (1)]

$$\left| \frac{d\theta}{dt} \right| \tau_e \approx 10^{-2} \quad \text{at } T = T_g. \quad (46)$$

This condition implies in agreement with the Kauzmann-Beaman rule^{2,3} that the temperature range of vitrification is located around the temperature $T_g \approx (2/3)T_m$ or $\theta_g \approx 2/3$ as it is, in fact, observed in Fig. 2.

After the completion of a cyclic cooling-heating process, the initial state of the system is reestablished, again. Consequently, we have $\oint d\xi = 0$. Here \oint denotes the integration over the whole cycle. It follows as a first consequence [see Eq. (44)] that the relation

$$\oint \frac{1}{q_{\theta}\tau}(\xi - \xi_e)d\theta = 0 \quad (47)$$

has to be fulfilled. Further, the inequality $(\xi - \xi_e) \geq 0$ holds in the whole course of the cooling process. Inside the vitrification interval, both the differences $(\xi - \xi_e)$ and the relaxation times increase with decreasing temperature, however, with very different rates: the relaxation times increase exponentially [see Eq. (45)] and the difference $(\xi - \xi_e)$ with a rate near a linear one (see Fig. 2). As a result from these considerations and Eq. (24) for the entropy production, we obtain a single maximum of the entropy production in cooling, shown in Fig. 3 by a full curve.

After completion of the cooling process, the initial state can be reestablished only if, in the course of the subsequent heating, the order parameter ξ becomes less than ξ_e at a

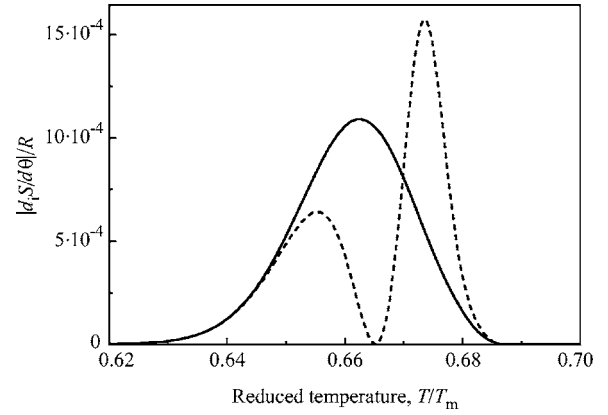


FIG. 3. Entropy production [Eq. (48)] in vitrification and devitrification in a cyclic cooling-heating run experiment. The entropy production has one maximum for cooling (full curve) and two maxima in heating processes (dashed curve).

certain value of temperature and then approaches ξ_e from below. It follows that, in heating runs, a point of intersection of the curves $\xi = \xi(p, T, q)$ and $\xi_e = \xi_e(p, T)$ has to exist. At this point, the curve $\xi = \xi(p, T, q)$ has—according to Eq. (44)—a minimum. At this minimum, the system is in equilibrium and the entropy production drops to zero [see Eq. (24)] being different from zero below and above this particular temperature. As a direct consequence, the entropy production, $(d_i S/dT)$, has two maxima in heating processes in the glass transition interval. This general result is illustrated in Fig. 3. Here the entropy production in cooling (showing one single maximum) is given by a full curve, while the two maxima of the entropy production in heating are given via a dashed curve. As evident from the above discussion, this result is valid independent of the value of the cooling and heating rates and of the particular model assumptions utilized here for the computation of Fig. 3: for any model of glass-forming melts employing one structural order parameter, where ξ_e is a monotonous function of temperature, the entropy production term has to have one maximum in cooling and two in heating.

Figure 4 shows the total entropy produced due to irreversible relaxation processes proceeding in the system in the glass transition interval. For the computations leading to Figs. 3 and 4 we write Eq. (24) in the form

$$\frac{d_i S}{d\theta} = \frac{G_e^{(2)}}{T_m \theta q_{\theta} \tau} (\xi - \xi_e)^2. \quad (48)$$

For the determination of $G_e^{(2)}$, we employed the relation [see Eq. (38)]

$$\begin{aligned} G_e^{(2)} &= \left. \frac{\partial^2 G}{\partial \xi^2} \right|_{\xi=\xi_e} = \left. \frac{\partial^2 G_{\xi}}{\partial \xi^2} \right|_{\xi=\xi_e} \\ &= RT_m \left[\frac{\theta}{\xi_e(1-\xi_e)^2} \left(1 + 2 \frac{\xi_e \ln \xi_e}{(1-\xi_e)} \right) \right], \end{aligned} \quad (49)$$

where ξ_e is determined via Eq. (39). Note that the product $(T_m \theta)$ cancels when Eqs. (48) and (49) are combined.

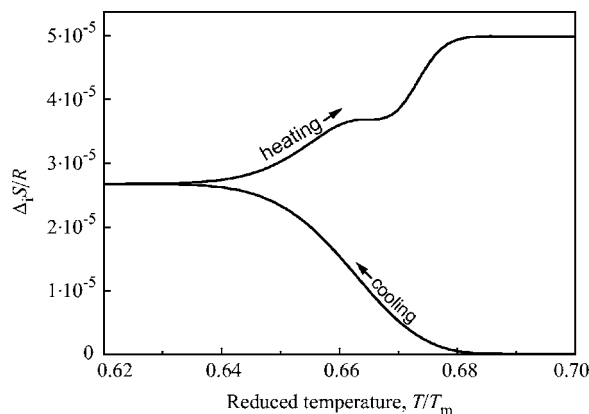


FIG. 4. Total entropy $\Delta_p S$ produced in the system in the cyclic cooling-heating process. In the cooling run, the entropy production becomes effective in the vitrification range, and it drops then to zero due to the large relaxation times. In the subsequent heating, again, entropy is produced in the same temperature range as in the cooling process. Note that the entropy produced in cooling is larger than the entropy generated in heating. This result is due to the difference in the values of $(\xi - \xi_e)$ in the glass transition interval for cooling and heating, respectively.

For an analytical analysis of the possible magnitude of the effect of entropy production on the thermodynamic functions, we can use the approximative result $G_e^{(2)} \cong RT/\xi_e$, derived here earlier [see the discussion following Eq. (40)]. Equation (48) can be written then in the form

$$\frac{d_i S}{d\theta} \cong \frac{R}{q_\theta \tau} \frac{(\xi - \xi_e)^2}{\xi_e}. \quad (50)$$

In the vicinity of the glass temperature, independent of the substance considered and the rate of change of temperature (or, more generally, the external control parameter), the relation $q_\theta \tau \cong \text{const}$ holds [see Eq. (1), again]. Consequently, the magnitude of the entropy production is determined, in general, basically by the ratio $(\xi - \xi_e)^2/\xi_e$ in the glass transition interval. Some consequences of this result will be discussed in Sec. VI.

C. Configurational contributions to the thermodynamic functions

As discussed in detail in the previous section, in the cyclic processes considered, the order parameter is a well-defined function of pressure, temperature, and the respective cooling and heating rates, i.e., $\xi = \xi(p, T, q)$ [see Eq. (43)]. The knowledge of this dependence allows us to determine the values of the thermodynamic functions. In particular, employing the model considerations outlined above, the configurational contributions to volume, enthalpy, entropy, internal energy, and Gibbs' free energy can be determined via Eqs. (32)–(38). For the specification of volume and internal energy in terms of the model employed, in addition, the dependence of the volume per particle of the liquid in the absence of holes, $v = v_0(p, T)$, has to be known. The kind of temperature course of the volume (and the internal energy) of the system under consideration in a cyclic cooling-heating process depends on the relative significance of two terms.

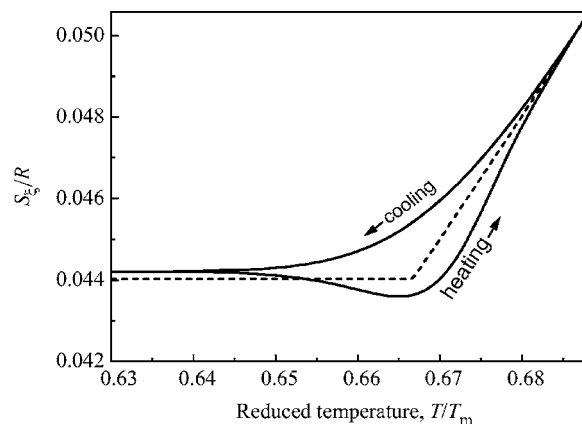


FIG. 5. Configurational contribution to the entropy S_ξ [Eq. (36)] determined in accordance with Simon's model of vitrification (dashed curve) and the model of a continuous transition as employed here (full curve). Note that in the latter case the entropy behaves differently in cooling and heating runs due to differences in the temperature dependences of the structural order parameter, $\xi(p, T, q)$, for cooling and heating (see Fig. 2).

Indeed, employing Eq. (32), we obtain (at constant pressure) the following expression for the changes of the volume in dependence on temperature:

$$\frac{dV(p, T, \xi)}{dT} = \left(\frac{\partial V}{\partial T} \right)_{p, \xi} + \left(\frac{\partial V}{\partial \xi} \right)_{p, T} \frac{d\xi}{dT} \cong N_A \left(\frac{\partial v_0(p, T)}{\partial T} + v_0(p, T) \frac{d\xi}{dT} \right)_p. \quad (51)$$

The temperature dependences of the configurational contributions to the entropy [Eq. (36)] and Gibbs' free energy [Eq. (38)] are shown in Figs. 5 and 6 both for Simon's model [i.e., $\xi = \xi_e$ for $T \geq T_g$ or $\theta \geq (2/3)$ and $\xi = \xi(T_g)$ for $(1/2) \leq \theta < (2/3)$] and the model of a continuous transition to the glass as discussed here [$\xi = \xi(p, T, q)$]. The configurational contribution to the enthalpy is not drawn separately since its dependence on temperature repeats the respective curves drawn for the structural order parameter ξ shown in Fig. 2. A

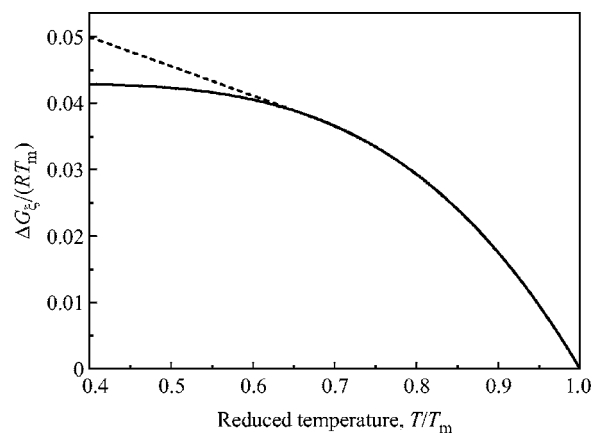


FIG. 6. Configurational contribution to Gibbs' free energy, $\Delta G_\xi = G_\xi(T) - G_\xi(T_m)$ [Eq. (38)], determined in accordance with Simon's model of vitrification and the model of a continuous transition as employed here. The full curve corresponds to the state of the metastable liquid. For the parameters considered and in the scale used for the presentation, the results of Simon's model and of the generic model of glass transition, employed for the analysis in the present contribution, coincide and are given by a dashed curve.

comparison of Figs. 4 and 5 shows that—at least for the model parameters considered—the entropy production term is small as compared with the characteristic values of the structural contributions to the entropy shown in Fig. 4. This result is reflected also in Fig. 6 showing that the Simon model and the model of the continuous transition employed here lead for the present model and parameter values to practically identical results for the configurational contributions to the Gibbs free energy. A general estimate of the possible magnitude of the effect of entropy production, based on Eq. (50), will be performed in a forthcoming paper;²² some first conclusions in this respect are included in Sec. VI.

Finally, the specific heat along the path, given by $\xi = \xi(p, T, q)$, is a function of pressure, temperature, and the order parameter, i.e., $C_p = C_p(p, T, \xi)$. We have, by definition,

$$C_p(p, T, \xi) = \frac{dQ}{dT}. \quad (52)$$

From the first law of thermodynamics [$dU = dQ - pdV$; Eq. (5)] and the definition of the enthalpy, $H = U + pV$, we obtain

$$dH = dQ + Vdp, \quad (53)$$

resulting, with the condition $p = \text{const}$, in

$$dH = C_p(p, T, \xi)dT. \quad (54)$$

In a more extended form, Eq. (54) can be written as the sum of two terms (see Refs. 2, 5, and 7),

$$C_p(p, T, \xi) = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T} \right)_{p, \xi} + \left(\frac{\partial H}{\partial \xi} \right)_{p, T} \frac{d\xi}{dT}. \quad (55)$$

The first term on the right hand side of the above equation reflects the contribution to the specific heat due to thermal motion of the molecules (e.g., the phononic part), while the second term refers to configurational contributions.

Employing the model of glass-forming melts discussed above, the configurational contribution to the specific heat $C_{p, \xi}$ is given with Eq. (34) by

$$C_{p, \xi} = \left(\frac{\partial H_\xi}{\partial \xi} \right)_{p, T} \frac{d\xi}{dT} = \chi_1 \Delta H_{ev}(T_m) \frac{d\xi}{dT}. \quad (56)$$

In the model of vitrification, developed by Simon, the glass-forming system remains in a metastable state until a certain temperature, T_g , is reached in the cooling process [i.e., $\xi = \xi_e$ for $T \geq T_g$ or $\theta \geq (2/3)$]. At this temperature, the system becomes frozen-in and the structural order parameter does not change anymore in the further cooling process [i.e., $(d\xi/dT) = 0$ for $T \leq T_g$ or $\theta \leq (2/3)$]. The configurational contribution, $C_{p, \xi}$, to the specific heat resulting from processes of structural reorganization has, consequently, the form

$$C_{p, \xi}^{(\text{Simon})} = \begin{cases} \chi_1 \Delta H_{ev}(T_m) (d\xi_e/dT) & \text{for } T_g \leq T \leq T_m \\ 0 & \text{for } 0 \leq T < T_g, \end{cases} \quad (57)$$

with [cf. Eq. (39)]

$$\frac{d\xi_e}{dT} = \chi \left(\frac{T_m}{T^2} \right) \frac{\xi_e(1 - \xi_e)^3}{1 - \xi_e + 2\xi_e \ln \xi_e} \quad (58)$$

or

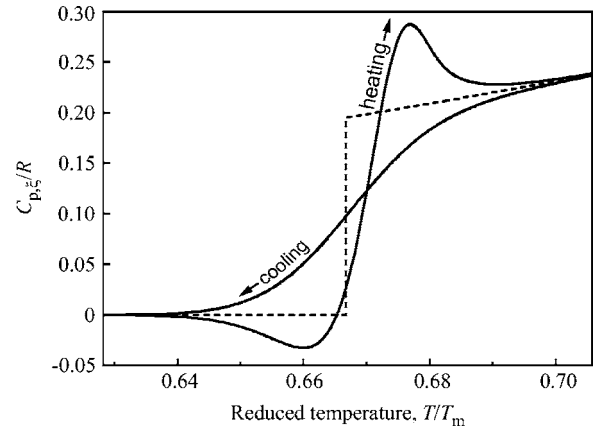


FIG. 7. Configurational contribution, $C_{p, \xi}(p, T, \xi)$, to the specific heat, $C_p = C_p(p, T, \xi)$, as obtained via Simon's model approach (dashed curve) and the model of a continuous transition as employed here (full curve). Note that, in describing vitrification more appropriately in terms of a continuous transition, the specific heats turn out to be different for cooling and heating runs (see experimental data shown in Fig. 8).

$$\frac{d\xi_e}{d\theta} = \frac{1}{\chi} \frac{\xi_e (\ln \xi_e)^2}{(1 - \xi_e + 2\xi_e \ln \xi_e)(1 - \xi_e)}. \quad (59)$$

In contrast, considering vitrification as a continuous transition from a metastable to a frozen-in state, we have generally

$$C_{p, \xi} = \chi_1 \Delta H_{ev}(T_m) \frac{d\xi}{dT} \cong \chi RT_m \frac{d\xi}{dT}, \quad T_0 \leq T \leq T_m. \quad (60)$$

Moreover, the configurational contribution to the specific heat becomes also different in dependence on whether we consider cooling or heating processes. Results of the theoretical computations of the configurational contributions to the specific heats are shown in Fig. 7. In Fig. 8, experimental results are presented, giving a confirmation of the theoretical considerations outlined here. It is evident that experimental data for the heat capacity of glass-forming systems in cooling and heating behave qualitatively in the same way as shown in Fig. 7 representing the results of theoretical computations. This coincidence is considered by us as one of the straightforward verifications of the theoretical approach employed here.

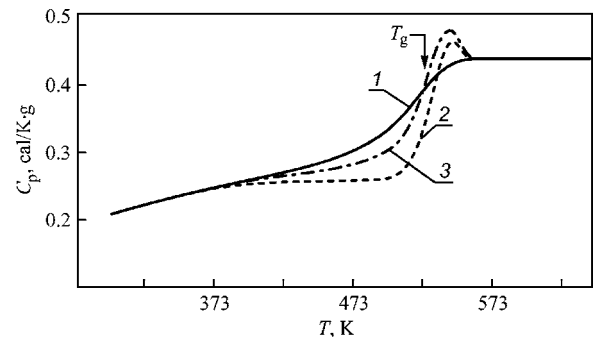


FIG. 8. Experimental heat capacity curves of B_2O_3 melts upon vitrification after Thomas and Parks (Ref. 23) (see also Ref. 24): (1) cooling run curve, (2) heating curve after slow cooling run, and (3) heating curve after fast cooling run. Note that in this figure the full specific heat is shown [see Eq. (55)] and not only the configurational contribution presented in Fig. 7.

D. General results

So far, we have determined the thermodynamic functions based on the knowledge of the temperature dependence of the structural order parameter, $\xi = \xi(p, T, q)$, employing results of statistical-mechanical model considerations. Alternatively, one can determine the thermodynamic functions based on measurements of the specific heats at a given rate of cooling or heating. For example, the enthalpy can be determined then via Eq. (54). Similarly, we obtain for the entropy [see Eq. (2)]

$$C_p(p, T, \xi) = \frac{dQ}{dT} = T \frac{d_e S}{dT} = T \frac{dS}{dT} - T \frac{d_i S}{dT}$$

$$\Rightarrow T \frac{dS}{dT} = C_p(p, T, \xi) + T \frac{d_i S}{dT}. \quad (61)$$

Furthermore employing the heating and cooling law, $dt = dT/q$, along with Eq. (24) we arrive at

$$dS = \frac{C_p(p, T, \xi)}{T} dT + \frac{G_e^{(2)}}{Tq\tau} (\xi - \xi_e)^2 dT. \quad (62)$$

Remember that the structural order parameter ξ can be expressed in all equations given above, Eqs. (52)–(62), uniquely via pressure, temperature, and cooling and heating rates, respectively. The respective dependences differ, in general, for cooling and heating (i.e., for negative and positive values of the heating rate q). Consequently, the thermodynamic functions are different in cooling and heating as well. Having at one's disposal the dependence $S = S(p, T, \xi)$ or [with Eq. (43)] $S = S(p, T, q)$, one can immediately compute also other thermodynamic parameters such as the change of the volume of the system with respect to temperature via

$$\left(\frac{\partial V}{\partial T} \right)_{p, \xi} = - \left(\frac{\partial S}{\partial p} \right)_{T, \xi}. \quad (63)$$

Completing the analysis, we finally derive some integral characteristics of the cyclic processes analyzed which do not depend on particular properties of the systems under consideration but are consequences from the basic laws of thermodynamics. Since we start at and return to equilibrium states, the thermodynamic state functions such as entropy, enthalpy, and Gibbs' free energy recover after the completion of the cyclic process the same values they had at the starting point. In this way, we may write, for example,

$$\oint dS = \oint d_e S + \oint d_i S = 0. \quad (64)$$

Since

$$\oint d_i S \geq 0 \quad (65)$$

holds, we get

$$\oint d_e S = \oint \frac{dQ}{T} = \oint \frac{C_p(p, T, \xi)}{T} dT \leq 0. \quad (66)$$

Note that the specific heat depends not only on (the constant) pressure and (the changing in time) temperature but also on

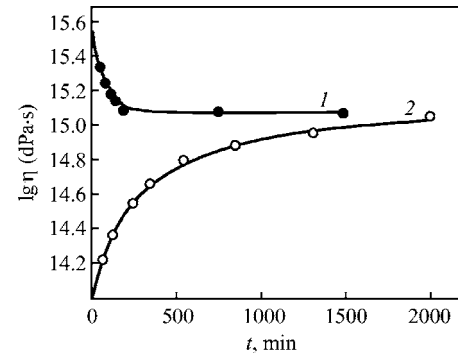


FIG. 9. Viscosity vs time curves for two samples of a silicate glass with the same composition but different thermal histories heat treated at 486 °C [after Lillie (Ref. 25)]. Curve (1): Glass sample equilibrated at a lower temperature (478 °C). Curve (2): Glass sample transferred from temperatures considerably above 486 °C to room temperatures and brought to 486 °C afterwards. Note that in both cases from different sides the same equilibrium value of the viscosity is approached corresponding to the equilibrium value of the structural order parameter.

the structural order parameter ξ . Only for reversible cyclic processes, the equality sign in Eq. (66) holds, but this is not the case in vitrification, where cooling and heating are accompanied, in general, by nonequilibrium relaxation and entropy production processes.

Similarly, Eq. (53) yields (at assumed constancy of pressure)

$$\oint dH = \oint dQ = \oint C_p(p, T, \xi) dT = 0. \quad (67)$$

Furthermore, from Eq. (9) we obtain, with Eq. (6) and assuming, again, constancy of the pressure, the relation

$$- \oint dG = \oint S dT + \oint A d\xi = \oint S dT + \oint T d_i S = 0. \quad (68)$$

Since $\oint T d_i S \geq 0$ holds, we arrive at

$$\oint S dT \leq 0. \quad (69)$$

Note that all relations derived in this section are valid independent of any particular assumptions about cooling or heating rates employed in the realization of the cyclic processes discussed.

V. ON THE BEHAVIOR OF THE VISCOSITY AT THE GLASS TRANSITION

As already accounted for in analysis of the kinetics of relaxation, not only the thermodynamic parameters but also the kinetic parameters of glass-forming systems may depend on the structural order parameters. Experimental data, verifying this statement with respect to the viscosity, are presented in Fig. 9. As shown in the figure, isothermal relaxation processes, connected with changes of the structural order parameter, may result in variations of the viscosity, and the value of the viscosity at some given pressure and temperature may depend, in general, on the prehistory of the system. For this reason, the theoretical approach developed

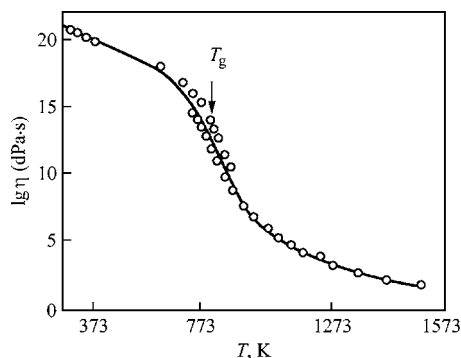


FIG. 10. Temperature dependence of the viscosity of a classical glass-forming melt: the change of the slope of the $\log \eta(T)$ curve upon vitrification for a soda-lime silicate glass in a very broad viscosity interval [after Winter's analysis (Ref. 27), based on experimental data of several authors].

is of essential significance for the comprehensive understanding not only of the thermodynamic parameters but also of the kinetic parameters of glass-forming melts in cooling and heating processes. This statement will be elaborated in more detail in the present section in application to viscosity as one of the basic kinetic parameters of glass-forming melts.

Assuming, again, the existence of only one structural order parameter, ξ , we may write generally the following expression for the temperature dependence of the viscosity (at constant pressure):

$$\frac{d\eta}{dT} = \left(\frac{\partial \eta}{\partial T} \right)_{\xi} + \left(\frac{\partial \eta}{\partial \xi} \right)_{T} \frac{d\xi}{dT}. \quad (70)$$

For systems in stable or metastable thermodynamic equilibrium, ξ is an unambiguous function of pressure and temperature. In general, ξ is a function also of the cooling rate. For this reason, near the glass transition temperature, equilibrium [here the derivative $(d\xi/dT)$ has to be determined for the curve $\xi = \xi_e(p, T)$] and nonequilibrium [here the derivative has to be determined for the curve $\xi = \xi(p, T, q)$ depending on cooling or heating rates] viscosities may be distinguished.

Explicitly, this effect is reflected by the Macedo-Litovitz equation²⁶

$$\eta(p, T, \xi) = \eta_0(p, T) \exp\left(\frac{U_a}{RT}\right) \exp\left(\frac{B}{\xi}\right). \quad (71)$$

Since, for cooling processes, $\xi_e \leq \xi$ holds, for cooling we have to expect a behavior as shown in Fig. 10 (see also Ref. 2). For heating, the order parameter behaves differently (see Fig. 2). For this reason, in heating runs we have to expect some kind of oscillatory approach of the viscosity to the equilibrium viscosity, i.e., the curve corresponding to the nonequilibrium viscosity will intersect the equilibrium curve and tend to this equilibrium curve with increasing temperature from above. A more detailed analysis of these effects is in progress.

By the way, the Macedo-Litovitz equation is in agreement with the expressions employed here for the relaxation time [see Eq. (29)]. Indeed, we can write the second term in the Macedo-Litovitz equation as

$$\frac{B}{\xi} = \frac{B}{\xi_e + (\xi - \xi_e)} = \frac{B}{\xi_e(1 + (\xi - \xi_e)/\xi_e)} \cong \frac{B}{\xi_e} \left(1 + \frac{\xi - \xi_e}{\xi_e} \right). \quad (72)$$

Consequently, the Macedo-Litovitz equation can be written approximately in the form

$$\eta(p, T, \xi) = \eta_0(p, T) \exp\left(\frac{U_a}{RT}\right) \exp\left(\frac{B}{\xi_e} \left(1 + \frac{\xi - \xi_e}{\xi_e} \right)\right), \quad (73)$$

in, at least, qualitative agreement with Eq. (29).

VI. RESULTS AND DISCUSSION

Any isothermal measurements of relaxation processes in glass-forming systems represent—in accordance with the basic laws of thermodynamics—a direct experimental proof that entropy production effects occur and have to be accounted for as an inherent feature of any glass transition. However, following Simon's model, the relevance of such effects in vitrification has been ignored so far widely both in theoretical and experimental investigations. For this reason, direct experimental analyses allowing one to analyze the effect of entropy production and its consequences for the understanding of the properties of glasses are relatively scarce. As far as they are known to us, they are discussed in detail in a forthcoming study²² devoted to an outline of direct experimental verifications of the theoretical concepts presented here. Anyway, experimental examples already mentioned in the present paper [possibility of derivation of the Frenkel-Kobeko and Bartenev-Ritland equations based on Eq. (1), qualitative identity of experimental and theoretical $C_p(T)$ curves (see Figs. 7 and 8), possibility of a straightforward theoretical interpretation of the Prigogine-Defay ratio,⁵ possibility of interpretation of peculiarities in the temperature dependence of the viscosity near and below T_g (see Figs. 9 and 10), the mere existence of isothermal relaxation processes, etc.] give a convincing proof that (i) vitrification has to be explained theoretically as a process proceeding in some finite interval of the external control parameters, (ii) the vitrification interval is characterized by an interplay of relaxation and change of external control parameters which determines the properties of the glasses, (iii) the freezing-in process is accompanied by entropy production, and (iv) the theoretical approach developed here gives an appropriate tool to treat such effects.

Of course, a more detailed direct experimental and theoretical analysis of entropy production and its effect on the properties of the resulting glasses for different classes of glass-forming melts is highly desirable. One possible circle of analyses could consist here in the measurement of heat effects in isothermal relaxation. A more straightforward circle of experiments allowing one to verify directly the theoretical predictions outlined here consists in the analysis of thermal effects of relaxation in cyclic heating and cooling processes. Here, as one of the possible tasks, a direct proof of the general thermodynamic consequences outlined in Sec. IV D could be performed. Another topic of interest is, to our opinion, the analysis of the magnitude of entropy production effects in dependence on the rate of change of the external

control parameters. According to the theoretical concepts followed in the paper, the glass transition temperature T_g is defined by the relation [cf. Eq. (1)]

$$q_\theta \tau(T_g) \cong \text{const}, \quad \theta = \frac{T}{T_m}, \quad q_\theta = \frac{d\theta}{dt}. \quad (74)$$

In verbal form, the vitrification temperature is reached, when the characteristic relaxation times are comparable in magnitude with the characteristic times of change of temperature.² It follows as one consequence that—describing the viscosity via the Vogel-Fulcher-Tammann equation—the glass transition temperature has to be always located above the Kauzmann temperature, since the assumption $T_g = T_0$ would lead to a zero cooling rate, i.e., to a process which cannot be realized. On the other hand, Eq. (50), supplemented by the definition of the glass temperature [Eqs. (1) and (74)], shows that the rate of approach of the structural order-parameter temperature ξ to its equilibrium value ξ_e is, near the glass transition temperature, independent of the cooling rate. For this reason, with increasing cooling rates higher values of the difference $(\xi - \xi_e)$ are expected to be found, in general, near T_g : the rate of approach of ξ to ξ_e is constant near T_g but the rate of change of ξ_e increases with increasing cooling rates (similar considerations can be made also with respect to the heating runs). As the result, an increased effect of the entropy production term has to be expected, in general, with increasing rates of change of the control parameters. Vice versa, with a decrease of the cooling rate the entropy production term should lose its importance. This result is in qualitative agreement with expectations that near the Kauzmann temperature an ideal glass transition has to take place, where entropy production terms are negligible. On the other hand, increasing values of the rate of change of the control parameters may reduce the width of the vitrification interval. Due to both above mentioned circumstances a more detailed analysis is required in order to arrive at some final conclusion, whether the theoretical concepts employed reconfirm the mentioned expectation concerning possible ideal glass transitions or not.

In the present analysis, we considered mainly cyclic processes of vitrification and devitrification, where both cooling and heating proceed with the same constant absolute value of the rate of change of temperature. Most of our conclusions retain their validity if we assume that this condition of constant heating or cooling rate is not fulfilled, but the temperature is a strictly monotonic function of time in both heating and cooling. However, the respective results are harder to interpret and in discussing new effects, one should always start, as we did here, with the simplest realizations. In addition, we considered cyclic processes, where the initial state is always reestablished after the completion of the process of cooling and subsequent heating. Provided that one starts the cycle at temperatures inside the vitrification interval, ($T_g^- \leq T_g \leq T_g^+$), then the behavior of the system should depend on the number of the cycle in a series of cyclic heating-cooling processes. It would be of interest to perform also experiments in this respect and to compare them with the theoretical predictions obtained in the framework of the theory presented here.

The theoretical approach developed in the present analysis leads to a variety of additional results in the theoretical interpretation of vitrification. Some of them are discussed in Refs. 5 and 22. However, the potential applications of the theoretical concepts outlined here are expected to be of much wider applicability (see, e.g., Refs. 28–30) and will be explored in future analyses.

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- ¹F. Simon, Z. Anorg. Allg. Chem. **203**, 219 (1931).
- ²I. Gutzow and J. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization* (Springer, Berlin, 1995).
- ³I. Gutzow, D. Ilieva, F. Babalievski, and V. Yamakov, J. Chem. Phys. **112**, 10941 (2000).
- ⁴I. Gutzow, Ts. Grigorova, I. Avramov, and J. W. P. Schmelzer, *Proceedings of the XIXth International Congress on Glass* [Phys. Chem. Glasses **43C**, 477 (2001)].
- ⁵J. W. P. Schmelzer and I. Gutzow, J. Chem. Phys. (submitted).
- ⁶Th. de Donder and P. van Rysselberghe, *Thermodynamic Theory of Affinity* (Stanford University Press, Stanford, 1936).
- ⁷I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans, London, 1954).
- ⁸R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953); Proc. R. Soc. London, Ser. A **217**, 26 (1953).
- ⁹C. 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, and J. A. Wilder, Ann. N.Y. Acad. Sci. **279**, 15 (1976).
- ¹⁰C. T. Moynihan and P. K. Gupta, J. Non-Cryst. Solids **29**, 143 (1978).
- ¹¹S. V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State* (CRS, London, 1994).
- ¹²L. D. Landau and E. M. Lifshitz, *Course in Theoretical Physics* (Akademie, Berlin, 1969), Vol. 5.
- ¹³R. Kubo, *Thermodynamics* (North-Holland, Amsterdam, 1968).
- ¹⁴H. B. Callen, *Thermodynamics: Physical Theories of Equilibrium Thermodynamics and Irreversible Thermodynamics* (Wiley, New York, 1963).
- ¹⁵R. Haase, *Thermodynamik der Irreversiblen Prozesse* (D. Steinkopff, Darmstadt, 1963).
- ¹⁶J. Möller (unpublished).
- ¹⁷S. Glasstone, H. Laidler, and H. Eyring, *The Theory of Rate Processes* (Princeton University Press, New York, 1941).
- ¹⁸I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Thomas, Springfield, IL, 1955).
- ¹⁹I. Gutzow, I. Avramov, and K. Kästner, J. Non-Cryst. Solids **123**, 97 (1990).
- ²⁰M. V. Vol'kenstein and O. B. Ptizyn, JETP (USSR) **26**, 2204 (1956).
- ²¹W. I. Bragg and E. J. Williams, Proc. R. Soc. London, Ser. A **145**, 699 (1934).
- ²²I. Gutzow, J. Möller, and J. W. P. Schmelzer (unpublished).
- ²³S. B. Thomas and G. S. Parks, J. Chem. Phys. **35**, 2091 (1931).
- ²⁴G. W. Morey, *The Properties of Glass* (Reinhold, New York, 1954), p. 212.
- ²⁵H. R. Lillie, J. Am. Ceram. Soc. **16**, 619 (1933).
- ²⁶B. Macedo and T. A. Litovitz, J. Chem. Phys. **42**, 245 (1965).
- ²⁷A. Winter, Verres Refract. **7**, 217 (1953).
- ²⁸I. Gutzow, B. Petroff, S. V. Todorova, and J. W. P. Schmelzer, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer, G. Röpke, and V. B. Priezhev (Joint Institute for Nuclear Research, Dubna, 2005).
- ²⁹R. Feistel and W. Wagner, J. Phys. Chem. Ref. Data **35**, 1 (2006).
- ³⁰R. Feistel and S. Feistel, in *Irreversible Prozesse und Selbstorganisation*, edited by L. Schimansky-Geier, H. Malchow, and Th. Pöschel (Logos-Verlag, Berlin, 2006).