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Dependence of the width of the glass transition interval on cooling and heating rates

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In a preceding paper [J. W. P. Schmelzer, *J. Chem. Phys.* **136**, 074512 (2012)], a general kinetic criterion of glass formation has been advanced allowing one to determine theoretically the dependence of the glass transition temperature on cooling and heating rates (or similarly on the rate of change of any appropriate control parameter determining the transition of a stable or metastable equilibrium system into a frozen-in, non-equilibrium state of the system, a glass). In the present paper, this criterion is employed in order to develop analytical expressions for the dependence of the upper and lower boundaries and of the width of the glass transition interval on the rate of change of the external control parameters. It is shown, in addition, that the width of the glass transition range is strongly correlated with the entropy production at the glass transition temperature. The analytical results are supplemented by numerical computations. Analytical results and numerical computations as well as existing experimental data are shown to be in good agreement. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775802>]

I. INTRODUCTION

The analysis of the properties of glasses and of the dependence of their properties on the way they are formed is a problem of intensive current research with a variety of even partially not explored so far technological applications.^{1,2} The glass transition, the transition of a system being initially in a stable or metastable thermodynamic equilibrium state to a frozen-in non-equilibrium state, the glass, is a kinetic phenomenon and by this reason, kinetic criteria have to be employed in order to describe the glass transition and the properties of the resulting from such process glasses. This transition is most frequently so far performed by changes of temperature but a variety of other control parameters like pressure or external fields can be utilized for such purposes as well.^{1,2} Similarly to the situation discussed here, kinetic criteria of glass transition can be formulated for the case that the system is brought into the glassy state by a variation of other external control parameters or in the analysis of dynamic glass transitions.³

In a preceding paper,³ an overview on the spectrum of different historically developed kinetic criteria of glass transition has been given and a general model-independent kinetic criterion of glass formation, respectively, devitrification was developed. This general criterion contains the mentioned spectrum of criteria proposed earlier as limiting cases or consequences. As one of the results of this analysis, the dependence of the glass transition temperature at cooling and heating processes on external pressure and similar effects have been theoretically described in Ref. 3. As discussed in detail as well in the mentioned paper, different kinetic criteria of glass formation have been employed in the past in order to develop estimates of the dependence of the glass transition temperature on cooling and heating rates. Such relations are

commonly denoted as Bartenev-Ritland equations¹⁻³ in honor of the men^{4,5} which have performed such analysis for the first time.

In addition to the knowledge of the glass transition temperature also the dependence of the width of the glass transition interval on cooling and heating rates (or the rates of change of other control parameters employed) is of major interest. From experimental investigations at conventional cooling rates it has been found that, for example, for silicate glasses $(T_g^{(+)} - T_g^{(-)}) \cong 50$ K holds while for organic and polymer glasses frequently $(T_g^{(+)} - T_g^{(-)}) \cong 20$ K (cf., Ref. 2, page 55) is observed. Generally, for typical glass-formers estimates of the width of the glass transition range for cooling processes of the form

$$(T_g^{(+)} - T_g^{(-)}) \cong \left(\frac{1}{10} - \frac{1}{20} \right) T_g, \quad (1)$$

can be made (cf., Ref. 2, Eq. (5.56)). In above relations, T_g is the glass transition temperature while $T_g^{(+)}$ and $T_g^{(-)}$ are the upper and lower limits of the glass transition range. As far as we are aware, a theoretical analysis of the dependence of the upper and lower limits and the width of the glass transition interval on cooling and heating rates is missing so far. The development of theoretical methods of determination of these parameters is the aim of the present analysis.

In the present paper, we derive estimates of the upper and lower boundaries, $T_g^{(+)}$ and $T_g^{(-)}$, and of the width of the glass transition interval. In this analysis, we employ the general criterion of glass-formation formulated by us in Ref. 3. Such analysis is of interest per se and even more important taking into account that the glass transition is investigated presently both experimentally (such experiments are feasible, now, for cooling and heating rates in the range between 10^{-4} K/s up

to 10^5 K/s^{6,7}) and theoretically^{8,9} in wide ranges of cooling and heating rates, i.e., at rates of change of the external control parameters exceeding considerably the conventional rates realized earlier.

The analysis presented here is performed at a general level avoiding widely simplifying assumptions (Sec. II) in the derivation of the basic results. In the analysis of special applications, here we assume that cooling and heating proceeds with the same absolute value of the rate of change of temperature and that the relaxation time depends mainly on pressure and temperature and only weakly on the structural order parameter. Generalizations can be performed straightforwardly based on the general methods outlined here. Some elements and results of our analysis are similar to dependencies used or obtained in Refs. 10–13. Latter analysis is, however, developed based on a different starting point and directed to a different problem, the determination of the glass transition temperatures in cooling as compared to heating and the differences of both these quantities. In order to test our results, for a model system numerical computations of the width of the glass transition range in dependence on cooling and heating rates are performed (Sec. III). Analytical results and numerical computations will be shown to be in good agreement. In Sec. IV an alternative method of determination of the width of the glass transition interval will be discussed based on the analysis of the expression for the entropy production. A discussion of the results and further possible developments (Sec. V) completes the paper.

II. DETERMINATION OF THE BOUNDARIES AND THE WIDTH OF THE GLASS TRANSITION INTERVAL

A. General relations

In reconsidering the kinetic definition of the glass transition temperature, we developed first briefly in Ref. 14 and in an extended form in³ a model-independent formulation of the glass transition criterion. In this general model-independent approach, we introduced similarly to the characteristic relaxation time, τ_R , for the evolution of the structural order parameter, ξ , defined via (cf., e.g., Refs. 1, 2, 15, and 16),

$$\frac{d\xi}{dt} = -\frac{1}{\tau_R(p, T, \xi)}(\xi - \xi_e), \quad (2)$$

a characteristic time scale of change of temperature, τ_T , as

$$\frac{dT}{dt} = -\frac{1}{\tau_T}T, \quad \tau_T = \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \right\}^{-1}. \quad (3)$$

Here p is the pressure, T is the temperature, ξ_e the equilibrium value of the structural order parameter, and t the time. So, writing the expressions for the change of temperature and change of the structural order parameter in terms of the same laws, the respective characteristic time scales can be then introduced and compared directly.

According to Eq. (3), for any given value of the cooling or heating rate, $q = (dT/dt)$, we can consequently also determine a characteristic time of change of temperature, τ_T . The criterion for glass-formation is given by the condition that both

time scales coincide widely,³ i.e.,

$$T_g : \quad \tau_R \cong \tau_T \quad \Rightarrow \quad \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\}_{T=T_g} \cong 1. \quad (4)$$

Indeed, as stressed in detail in Ref. 3, classical equilibrium thermodynamics implies (as one of the conditions of its applicability) the fulfillment of the conditions $\tau_R \ll \tau_T$ (or $(\tau_R/\tau_T) = \alpha^{(+)} \ll 1$) while in the frozen-in non-equilibrium state, the glass, the inequality $\tau_R \gg \tau_T$ (or $(\tau_R/\tau_T) = \alpha^{(-)} \gg 1$) holds. Equation (4) specifies thus by necessity the transition region between equilibrium liquid and glass for the case that the glass transition is induced by a change of temperature.

Proceeding in this way, the upper ($T_g^{(+)}$) and lower ($T_g^{(-)}$) limits of the glass transition range can be defined then similarly to Eq. (4) as

$$T_g^{(+)} : \quad \tau_R \cong \alpha^{(+)}\tau_T \quad \Rightarrow \quad \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\}_{T=T_g^{(+)}} \cong \alpha^{(+)} \ll 1, \quad (5)$$

$$T_g^{(-)} : \quad \tau_R \cong \alpha^{(-)}\tau_T \quad \Rightarrow \quad \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\}_{T=T_g^{(-)}} \cong \alpha^{(-)} \gg 1, \quad (6)$$

by assigning appropriate values to the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$. For any given relaxation law, Eqs. (4), (5), and (6) determine the dependence of the glass transition temperature, T_g , and the upper, $T_g^{(+)}$, and lower, $T_g^{(-)}$, boundaries of the glass transition range by similar dependencies. Moreover, since the criteria determining the boundaries of the glass transition interval depend only on the absolute value of the cooling and heating rates, it follows, that – at a fixed absolute value of the rate of change of temperature (or any other appropriate external control parameters) – the boundaries of the glass transition region are identical for cooling and heating provided the relaxation time is a function only of pressure and temperature, i.e., that its dependence on the structural order parameter is weak. In the analysis of special cases, latter condition is always assumed to be fulfilled here.

An illustration of these general results is given in Fig. 1. The glass transition range is the region, where irreversible processes may proceed and the entropy production, d_iS , is not equal to zero. In the computations illustrated in Fig. 1, the relaxation time is supposed to be a function of pressure and temperature, exclusively, and cooling and heating rates are supposed to have the same constant absolute values (cf., Ref. 14 for the details). The dependence of the entropy production due to irreversible relaxation processes in the glass transition range is different for cooling and heating, however, the boundaries of the range where entropy production is different from zero coincide.

B. Qualitative estimates for different relaxation laws

While the glass transition temperature is determined by an identity of the type as given by Eq. (4), the relations for the determination of the boundaries of the glass transition interval, Eqs. (5) and (6), require for their application the

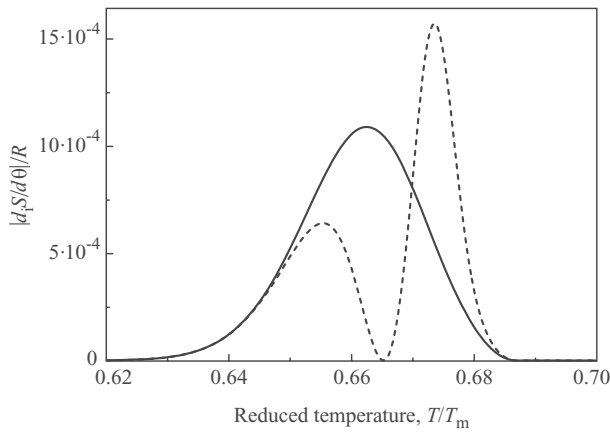


FIG. 1. Entropy production, $(d_i S/d\theta)$ (with $\theta = (T/T_m)$, T_m is the melting temperature and R the universal gas constant), in vitrification and devitrification in a cyclic cooling-heating run experiment with a constant absolute value of the rate of change of temperature. The entropy production has one maximum for cooling (full curve) and two maxima in heating processes (dashed curve), however, the boundaries of the glass transition interval (characterized by an entropy production tending to zero) are the same for cooling and heating processes provided, as assumed in addition that the dependence of the relation time on the structural order parameter is weak (for the details cf., Ref. 14 from which the figure is taken).

knowledge of the values of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$. In order to obtain a first qualitative insight into the course of the dependence of the boundaries and the width of the glass transition interval on cooling and heating rates, here we will proceed first in the following way. As estimates of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$ we will employ the relations

$$\alpha^{(+)} \cong 0.1, \quad \alpha^{(-)} \cong 10, \quad (7)$$

i.e., suppose that the system is frozen-in for $(\tau_R/\tau_T) \geq \alpha^{(-)} \cong 10$ and is found always in a metastable equilibrium state for $(\tau_R/\tau_T) \leq \alpha^{(+)} \cong 0.1$. Possible ways of a more precise specification of these parameters we will discuss here later. As will be evident from the results of the further analysis, the particular choice of these parameters affects the final results only slightly quantitatively. Consequently, proceeding in this way we can expect to get an at least qualitatively correct impression on the dependence of the width of the glass transition interval on cooling and heating rates. In order to avoid any misunderstanding, we would like to stress once again that in the subsequent consideration we will also describe methods allowing one to determine theoretically the values of these parameters. Such straightforward theoretical determination requires however much more information concerning the specific properties of the glass-forming systems under consideration as compared to the specification of the kinetic criteria expressed via Eq. (7).

The general relations, Eqs. (4)–(6), derived by us in the present paper, we will apply now utilizing two different relaxation laws, Arrhenius and Vogel-Fulcher-Tammann (VFT) relaxation. These relaxation laws are of particular significance for the description of relaxation processes in glass-forming melts.

1. Arrhenius relaxation

For Arrhenius-type relaxation processes,^{1,2} we have

$$\tau_R = \tau_0 \exp\left(\frac{U_0}{RT}\right) = \tau_0 \exp\left(\frac{A}{T}\right), \quad \frac{U_0}{R} = A = \text{constant}. \quad (8)$$

Here U_0 is some constant activation energy of structural relaxation, R is the universal gas constant, and τ_0 is a pre-factor, which can be approximated frequently by $\tau_0 = h/(k_B T)$, h being Planck's constant ($h = 6.63 \times 10^{-34}$ Js) and k_B the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K). Employing this relation, we get from Eqs. (4), (5), and (6)

$$\frac{1}{T_g} = \frac{1}{A} \ln\left(\frac{T_g}{\tau_0 q}\right), \quad q = \left|\frac{dT}{dt}\right|, \quad \tau_0 = \frac{h}{k_B T}, \quad (9)$$

$$\frac{1}{T_g^{(+)}} = \frac{1}{A} \ln\left(\frac{\alpha^{(+)} T_g^{(+)}}{\tau_0 q}\right), \quad (10)$$

$$\frac{1}{T_g^{(-)}} = \frac{1}{A} \ln\left(\frac{\alpha^{(-)} T_g^{(-)}}{\tau_0 q}\right). \quad (11)$$

In above relations, Eqs. (9), (10), and (11), τ_0 is a function of T_g , $T_g^{(+)}$, or $T_g^{(-)}$, respectively, i.e., T has to be replaced in dependence on the particular temperature value considered by T_g , $T_g^{(+)}$, or $T_g^{(-)}$. By the introduction of an appropriate dimensionless temperature, \tilde{T} , and dimensionless rate of change of temperature, \tilde{q} , via

$$\tilde{T} = \frac{T}{A}, \quad \tilde{q} = \frac{h}{k_B A^2} \left|\frac{dT}{dt}\right|, \quad (12)$$

an equation of the form

$$\frac{1}{\tilde{T}_g} = \ln \tilde{T}_g^2 - \ln \tilde{q} \quad (13)$$

is obtained from Eq. (9) for the dependence of the glass transition temperature on cooling and heating rates. Latter equation is commonly denoted as the Bartenev-Ritland equation.¹⁻⁵

Similar equations can be obtained as well from Eqs. (10) and (11) for the upper and lower boundaries of the glass transition range

$$\frac{1}{\tilde{T}_g^{(+)}} = \ln[(\tilde{T}_g^{(+)})^2 \alpha^{(+)}] - \ln \tilde{q}, \quad (14)$$

$$\frac{1}{\tilde{T}_g^{(-)}} = \ln[(\tilde{T}_g^{(-)})^2 \alpha^{(-)}] - \ln \tilde{q}.$$

As a consequence, we arrive at the following relation for the width of the glass transition interval

$$\frac{\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)}}{\tilde{T}_g^{(+)} \tilde{T}_g^{(-)}} = \ln \left[\left(\frac{\tilde{T}_g^{(-)}}{\tilde{T}_g^{(+)}} \right)^2 \left(\frac{\alpha^{(-)}}{\alpha^{(+)}} \right) \right]. \quad (15)$$

Explicitly, the difference $(\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)})$ in Eq. (15) does not depend on the rate of change of temperature, \tilde{q} , however, via the dependence of both $\tilde{T}_g^{(+)}$ and $\tilde{T}_g^{(-)}$ on the rate of change of temperature, implicitly it does.

For any set of values of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$, Eqs. (14) and (15) determine the values of the reduced temperatures $\tilde{T}_g^{(+)}$, $\tilde{T}_g^{(-)}$, \tilde{T}_g , and the width of the glass transition interval ($\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)}$) as functions of the reduced cooling rate, respectively, heating rate, \tilde{q} . The results are shown in Fig. 2. Employing the same approximation $\tilde{T}_g^{(+)}\tilde{T}_g^{(-)} \cong \tilde{T}_g^2$ as utilized in Refs. 10–13 in another context, this dependence can be approximately described by

$$\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)} \cong \tilde{T}_g^2 \ln\left(\frac{\alpha^{(-)}}{\alpha^{(+)}}\right), \quad (16)$$

or by

$$\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)} \cong \frac{\ln\left(\frac{\alpha^{(-)}}{\alpha^{(+)}}\right)}{(\ln \tilde{T}_g^2 - \ln \tilde{q})^2}. \quad (17)$$

It follows from Eqs. (16) and (17) (in agreement with the numerical computations as shown in Fig. 2) that the width of the transition range increases with increasing rate of change of temperature. It is evident as well that the approximation $\tilde{T}_g^{(+)}\tilde{T}_g^{(-)} \cong \tilde{T}_g^2$ employed in the derivation of Eqs. (16) and (17) leads to quantitatively correct results only for cooling & heating rates in the range $\tilde{q} \leq 10^0$.

With the specification Eq. (7) for the boundaries of the glass transition interval, the numerical factor $\ln(\alpha^{(-)}/\alpha^{(+)})$ is of the order of $\ln(\alpha^{(-)}/\alpha^{(+)}) \cong 4.6$. A redefinition via $\alpha^{(+)} \cong 0.01$ and $\alpha^{(-)} \cong 100$ leads only to a slight quantitative change resulting in $\ln(\alpha^{(-)}/\alpha^{(+)}) \cong 9.2$. Consequently, a change in the definition of the boundaries of the glass transition interval affects the results of the analysis only slightly quantitatively.

2. Vogel-Fulcher-Tammann relaxation

Let us assume now, as a second example, that the relaxation behavior is described by a Vogel-Fulcher-Tammann relaxation law,

$$\tau_R = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \quad B = \text{constant}, \quad (18)$$

which is of particular significance for the description of relaxation of glass-forming systems of different nature (cf., e.g. Refs. 1, 2, 17, and 18). For the further analysis, we introduce, now, similarly to Eq. (12) the notations

$$\tilde{T} = \frac{T}{B}, \quad \tilde{T}_0 = \frac{T_0}{B}, \quad \tilde{q} = \frac{h}{k_B B^2} \left| \frac{dT}{dt} \right|, \quad q = \left| \frac{dT}{dt} \right|. \quad (19)$$

In this case, we get from Eqs. (4), (5), and (6) instead of Eqs. (13)–(15),

$$\frac{1}{\tilde{T}_g - \tilde{T}_0} = \ln \tilde{T}_g^2 - \ln \tilde{q}, \quad (20)$$

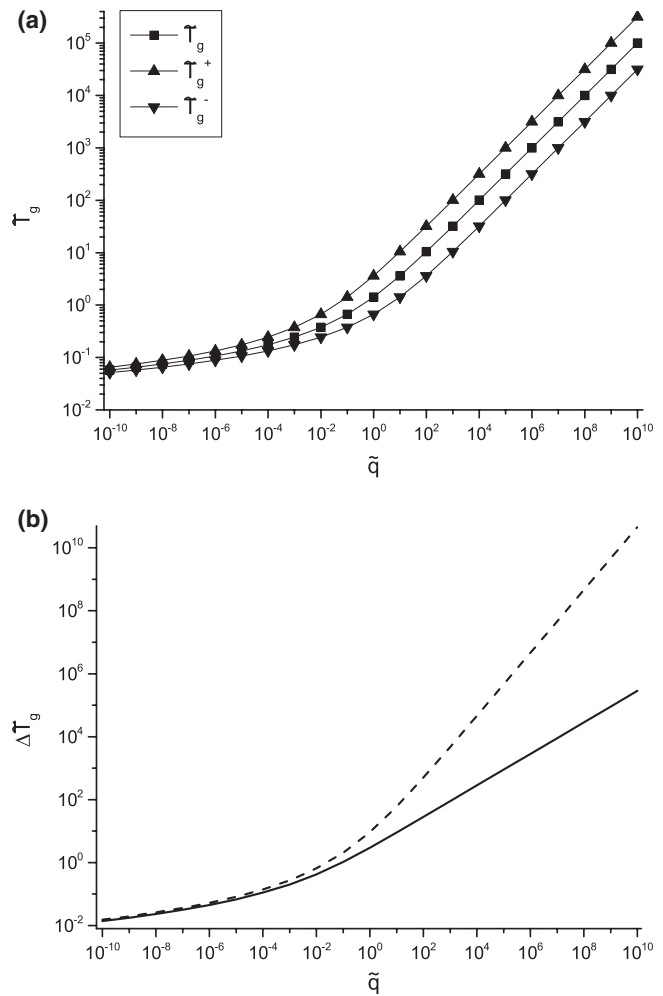


FIG. 2. Assuming the system relaxes via the Arrhenius law, for any set of values of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$, Eqs. (13)–(15) determine the values of the reduced temperatures \tilde{T}_g , $\tilde{T}_g^{(+)}$, $\tilde{T}_g^{(-)}$ and the width of the glass transition interval ($\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)}$) as functions of the reduced rate of change of temperature, \tilde{q} . The respective results are shown in the present figure employing the values of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$ as given by Eq. (7). The upper curve (Fig. 2(a)) shows the values of the reduced temperatures in dependence on cooling rate, the lower curves (Fig. 2(b)) show the width of the glass transition range in dependence on cooling rate computed via the correct dependencies (Eqs. (13)–(15), full curve) and via the approximation given by Eqs. (16) and (17) (dashed curve), respectively. It is evident that the approximation gives a qualitatively correct result for the whole spectrum of cooling rates employed, however, a quantitatively correct description is found only for sufficiently low cooling rates below $\tilde{q} \cong 10^0$.

$$\begin{aligned} \frac{1}{\tilde{T}_g^{(+)} - \tilde{T}_0} &= \ln[(\tilde{T}_g^{(+)})^2 \alpha^{(+)}] - \ln \tilde{q}, & \frac{1}{\tilde{T}_g^{(-)} - \tilde{T}_0} \\ &= \ln[(\tilde{T}_g^{(-)})^2 \alpha^{(-)}] - \ln \tilde{q}, \end{aligned} \quad (21)$$

$$\frac{\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)}}{(\tilde{T}_g^{(+)} - \tilde{T}_0)(\tilde{T}_g^{(-)} - \tilde{T}_0)} = \ln \left[\left(\frac{\tilde{T}_g^{(-)}}{\tilde{T}_g^{(+)}} \right)^2 \left(\frac{\alpha^{(-)}}{\alpha^{(+)}} \right) \right]. \quad (22)$$

Results of numerical computations of the values of the reduced temperatures $\tilde{T}_g^{(+)}$, $\tilde{T}_g^{(-)}$, \tilde{T}_g , and the width of the glass

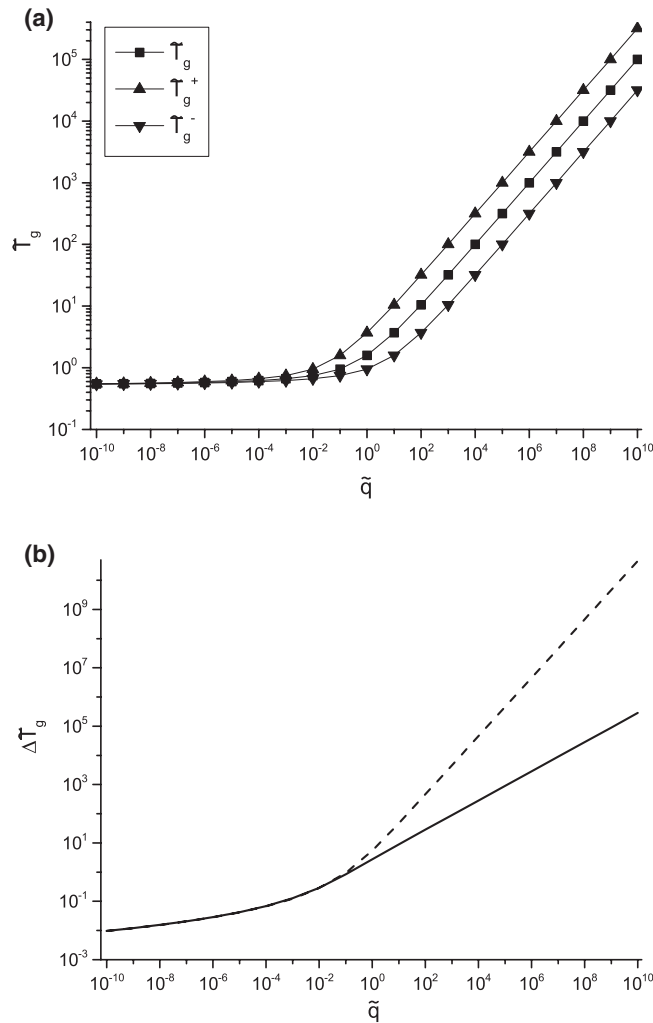


FIG. 3. Similar computations with similar results as shown in Fig. 2 for Arrhenius relaxation (cf., caption to Fig. 2) but here for the VFT-relaxation law as expressed in the paper via Eqs. (20)–(22) and the approximation, Eqs. (23) and (24).

transition interval ($\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)}$) as functions of the reduced cooling, respectively, heating rate, \tilde{q} , for a given set of values of the parameters are shown for this case in Fig. 3. Approximately, the dependence of the width of the glass transition interval on cooling, respectively, heating rates is described by the relations,

$$\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)} \cong (\tilde{T}_g - \tilde{T}_0)^2 \ln \left(\frac{\alpha^{(-)}}{\alpha^{(+)}} \right), \quad (23)$$

$$\tilde{T}_g^{(+)} - \tilde{T}_g^{(-)} \cong \frac{\ln \left(\frac{\alpha^{(-)}}{\alpha^{(+)}} \right)}{(\ln \tilde{T}_g^2 - \ln \tilde{q})^2}, \quad (24)$$

which are similar, respectively, identical to Eqs. (16) and (17).

A comparison of the results of analysis obtained for Arrhenius and Vogel-Fulcher-Tammann relaxation laws is given in Fig. 4. It is evident that deviations in the behavior occur mainly at relatively low cooling rates when vitrification proceeds sufficiently near to the Kauzmann temperature, T_0 .

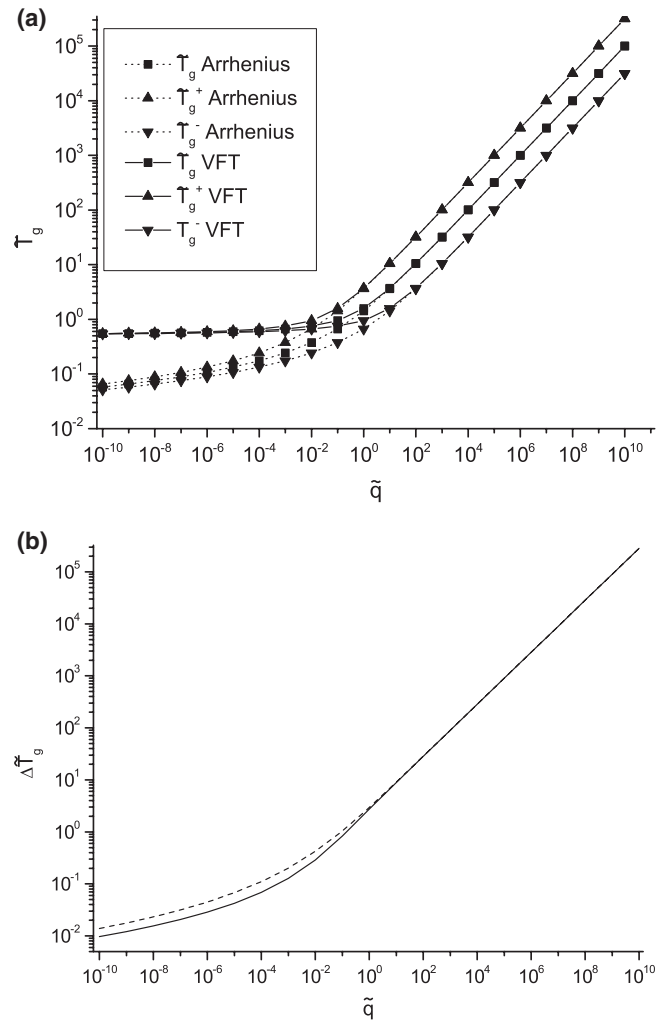


FIG. 4. Comparison of the results for the glass transition temperature and the width of the glass transition interval as obtained for Arrhenius (dotted curves) and VFT-relaxation (full curve, cf., Figs. 2 and 3, respectively).

III. COMPARISON WITH NUMERICAL MODEL COMPUTATIONS

A. Brief description of method of computations

In the present section, we compare the analytical results obtained here with the results of numerical computations of the glass transition for a model system characterized by one structural order parameter ξ . The change of this order parameter is described by the set of equations,

$$\frac{d\xi}{dt} = -\frac{1}{\tau_R}(\xi - \xi_e), \quad q = \frac{dT}{dt}, \quad (25)$$

resulting in the following equation for the determination of the structural order parameter:

$$\frac{d\xi}{dT} = -\frac{1}{q\tau_R}(\xi - \xi_e). \quad (26)$$

This equation allows one to describe the dependence of the structural order parameter on temperature for any given value of the rate of change of temperature. We assume here, as already pointed out, constancy of the cooling rate and that heating proceeds with the same absolute value of the rate of

change of temperature as the cooling process. The numerical computations have been performed for the case that relaxation is described by the VFT-equation. The detailed description of the model and the results of computations are outlined in Refs. 1, 2, 8, 9, and 14 and by this reason will not be repeated in detail here. We will merely make some comments concerning model parameters and the relation between the reduced temperature values employed here and in the numerical computations.

The numerical calculations within the mentioned model approach to the determination of the values of the glass transition interval at given constant cooling and heating rates are performed employing the following definitions of reduced dimensionless temperature, θ :

$$\theta = \frac{T}{T_m}, \quad \theta_0 = \frac{T_0}{T_m}, \quad q_\theta = \left| \frac{d\theta}{dt} \right| = \frac{1}{T_m} \left| \frac{dT}{dt} \right| = \frac{q}{T_m}. \quad (27)$$

Here T_m is the melting temperature of the system under consideration. The VFT relaxation law is written in the form

$$\tau_R = \tau_0 \exp \left(\left(\frac{U_a^*}{RT_m} \right) \frac{1}{\theta - \theta_0} \right), \quad \tau_0 = \frac{h}{k_B T}, \quad B' = \frac{U_a^*}{RT_m}. \quad (28)$$

In the above described analytical approach the following different reduced parameters have been introduced:

$$\tilde{T} = \frac{T}{B}, \quad \tilde{T}_0 = \frac{T_0}{B}, \quad \tilde{q} = \frac{h}{k_B B^2} \left| \frac{dT}{dt} \right|. \quad (29)$$

The VFT law was taken in the form,

$$\tau_R = \tau_0 \exp \left(\frac{B}{T - T_0} \right), \quad \tau_0 = \frac{h}{k_B T}. \quad (30)$$

Now in order to compare the data obtained analytically and by the numerical computations, we must derive relations between these reduced variables. First, for the VFT law, we get

$$\frac{B'}{\theta - \theta_0} = \frac{B}{T - T_0}, \quad \frac{T_m B'}{T - T_0} = \frac{B}{T - T_0}, \quad B = B' T_m. \quad (31)$$

For the Kauzmann temperature, T_0 , we immediately obtain (assuming T_0 being equal one half of the melting temperature, i.e., $T_0 = (1/2)T_m$),

$$T_0 = \frac{T_m}{2}, \quad \tilde{T}_0 = \frac{T_0}{B} = \frac{T_m}{2B'T_m} = \frac{1}{2B'}. \quad (32)$$

For cooling and heating rates, we have

$$\begin{aligned} \tilde{q} &= \frac{h}{k_B B^2} \left| \frac{dT}{dt} \right| = \frac{h}{k_B B^2} q = \frac{h}{k_B B^2} q_\theta T_m \\ &= \frac{h}{k_B B^2 T_m^2} q_\theta T_m = \frac{1}{B'^2} \frac{h}{k_B T_m} q_\theta. \end{aligned} \quad (33)$$

The parameters for numerical calculations were the following:

$$\frac{U_a^*}{RT_m} = B' = 5, \quad T_m = 750 \text{ K}, \quad q_\theta = 10^{-7} - 10^7 \text{ s}^{-1}. \quad (34)$$

Thus, the parameters which have to be employed here for the solution of the analytical relations, Eqs. (20)–(22), of the present analysis are

$$\tilde{T}_0 = \frac{1}{2B'} = \frac{1}{10} = 0.1, \quad \frac{h}{k_B T_m} \frac{1}{B'^2} \cong 2.56 \times 10^{-15} \text{ s}, \quad (35)$$

$$\tilde{q} = 2.56 \times 10^{-22} - 2.56 \times 10^{-13}. \quad (36)$$

With these in hand, we proceed to solving Eqs. (20)–(22), and obtain the sets of values \tilde{T}_g , $\tilde{T}_g^{(+)}$, and $\tilde{T}_g^{(-)}$. The way to derive then the values of θ is realized straightforwardly via

$$\tilde{T} = \frac{T}{B}, \quad \theta = \frac{T}{T_m}, \quad \theta = \frac{\tilde{T} B}{T_m} = \frac{\tilde{T} B' T_m}{T_m} = \tilde{T} B' = 5\tilde{T}. \quad (37)$$

Alternatively, in terms of the dimensionless temperature θ , Eqs. (20) and (21) read

$$\frac{1}{\theta_g - \theta_0} = \frac{T_m}{B} \left\{ \ln(\theta_g^2) - \left(\frac{h}{k_B T_m} \left| \frac{d\theta}{dt} \right| \right) \right\}, \quad (38)$$

$$\frac{1}{\theta_g^{(+)} - \theta_0} = \frac{T_m}{B} \left\{ \ln[(\theta_g^{(+)})^2 \alpha^{(+)}] - \ln \left(\frac{h}{k_B T_m} \left| \frac{d\theta}{dt} \right| \right) \right\}, \quad (39)$$

$$\frac{1}{\theta_g^{(-)} - \theta_0} = \frac{T_m}{B} \left\{ \ln[(\theta_g^{(-)})^2 \alpha^{(-)}] - \ln \left(\frac{h}{k_B T_m} \left| \frac{d\theta}{dt} \right| \right) \right\}. \quad (40)$$

Finally, in order to determine the width of the glass transition region based on the numerical computations, we have to develop some criterion concerning the definition of the boundaries of the glass transition interval. In other words, having a look at Fig. 1, we have to specify the value of the entropy production below which we can assume it to be equal to zero. We employ here the following two methods for this purpose: The methods for estimation of the glass transition region boundaries, $\theta_g^{(+)}$ and $\theta_g^{(-)}$, in dependence on q , employed in this work, are based on using the dependencies of structural order parameter, ξ , on temperature. A first straightforward procedure consists of computing the ratio $\xi_{cooling}/\xi_{heating}$ of the values of ξ , corresponding to the same temperatures at cooling, $\xi_{cooling}(T)$, and heating, $\xi_{heating}(T)$ runs, respectively. The dependencies of this ratio for three different values of rate of temperature change are presented on Fig. 5(a). At temperatures far from glass transition (in both states, i.e., liquid and glass), the value of $\xi_{cooling}/\xi_{heating}$ is equal to one. In the glass transition range, it is less than unity, the amount of deviation depending on the model parameters and the cooling and heating rate. As a direct way for estimating the values at the $\theta_g^{(+)}$ and $\theta_g^{(-)}$ the criterion of difference from unity of the ratio $\xi_{cooling}/\xi_{heating}$ ratio was used.

The disadvantages of the described procedure are clearly seen. They are, namely, the unnecessary dependence of the method on both cooling and heating runs in glass transition, and also the dependence of the glass transition range on the precision of computations of the ratios of different ξ -values. To avoid both these disadvantages, an alternative method was

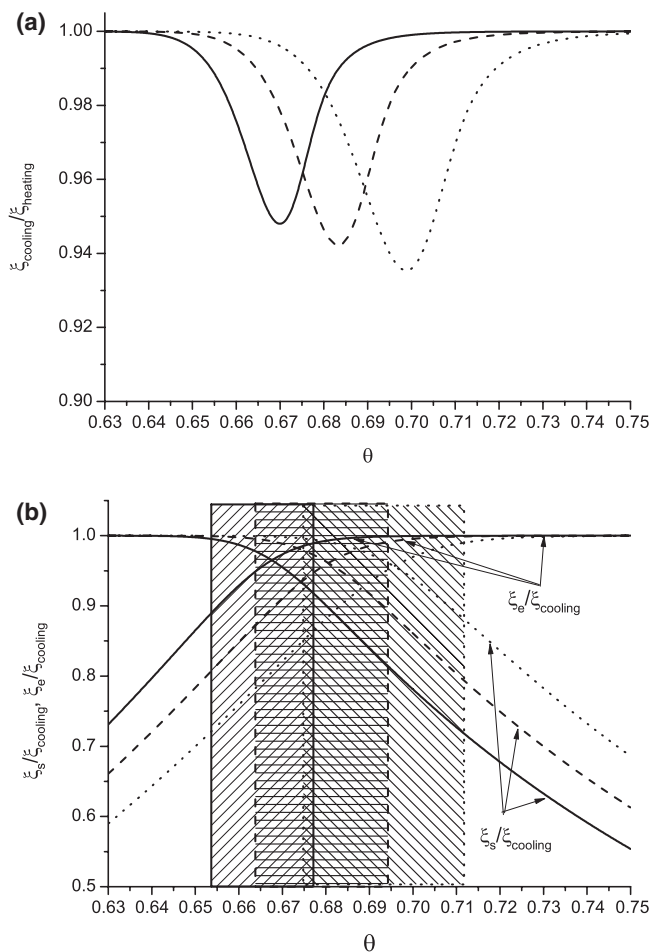


FIG. 5. Temperature dependencies of different ratios of the structural order parameter ξ employed to define the glass transition region for three values of cooling and heating rates ($q\theta$ is equal to 10^{-2} (full curve), 10^{-1} (dashed curve), and 1 s^{-1} (dotted curve), respectively). (a) Dependence of $\xi_{cooling}/\xi_{heating}$ and (b) of $\xi_e/\xi_{cooling}$ and $\xi_s/\xi_{cooling}$ on θ . The hatched rectangles represent the glass transition ranges, obtained with the use of the “1% criterion”.

developed. First, we shall use only the temperature dependencies of the systems properties during the cooling run. For this purpose, two different curves for obtaining $\theta_g^{(+)}$ and $\theta_g^{(-)}$ values are utilized. For the upper boundary of the glass transition range, it is the temperature dependence of the ratio of equilibrium value of structural order parameter, ξ_e , divided by $\xi_{cooling}$. To obtain the lower boundary, ξ_s , being the frozen-in value of the structural order parameter, is divided by $\xi_{cooling}$. The dependencies of these ratios on temperature for three different cooling rates are presented on Fig. 5(b). Each of the ratios is equal to one below (or above) the boundary it is invoked to define and does decrease in the glass transition range and further on. As a third method of specification of the width of the glass transition range, one could replace the entropy production in cooling by an inverted parabola utilizing a truncated Taylor expansion of the entropy production curve in the vicinity of the maximum up to second-order in temperature differences terms (cf., Fig. 1). This method will be discussed in detail in Sec. IV.

The criterion of deviation of the corresponding ratios from unity at the glass transition range boundaries is ex-

pressed as

$$\frac{\xi_e(\theta)}{\xi_{cooling}(\theta)} \Big|_{\theta=\theta_g^{(+)}} = \frac{\xi_s}{\xi_{cooling}(\theta)} \Big|_{\theta=\theta_g^{(-)}} = 1 - \beta. \quad (41)$$

Different values of β can be used and were tried in this work. Setting β equal to the precision of the numerical computations, 10^{-6} in our case, results in an inconsistently wide glass transition range. It should be mentioned that the obtained results with this value of β are similar to the results obtained with the first method of estimation of $\theta_g^{(+)}$ and $\theta_g^{(-)}$ values. Thus it is a qualitative indication of the fact that glass transition range is the same for a cooling and heating run at constant rate of temperature change. The value of β equal to $\beta = 0.1$ results in much lower values of the glass transition width, $\theta_g^{(+)} - \theta_g^{(-)}$, than the analytical (and “visual” one, from having a close look of ξ -curves) estimates. The value of β equal to $\beta = 0.01$ seems to be reasonable for the computations provided next and was used in this work. The criterion can be formulated as a 1% deviation of the respective ratios from their equilibrium (for upper boundary) and frozen-in (for lower boundary) values.

B. Results

The results of the computations obtained based on the first of the methods of determination of the glass transition boundaries are presented in Fig. 6. In this figure, the upper (θ_{max}) and lower (θ_{min}) values (a) and the width (b) of the glass transition interval are shown. In Fig. 7, both the first (a) and the second (b) method of specification of the boundaries of the glass transition interval are employed and specified as determined via the numerical model computations. In the figure, in addition, a comparison with the analytical results based on Eqs. (4)–(6) is given. The following conclusions can be derived from this figure: (i) Qualitatively, the results of determination of the glass transition temperature and the upper and lower boundaries of the glass transition range obtained via Eqs. (4)–(6) and the specification of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$ via Eq. (7) are in excellent agreement with the results of numerical model computations. (ii) Quantitatively, the agreement depends both on the method of determination of the boundaries of the glass transition interval and the glass transition temperature in the numerical computations and on the specific way of selection of the parameters $\alpha^{(+)}$ and $\alpha^{(-)}$ (for the way of determination of the glass transition temperature as employed in the numerical computations cf., Refs. 8 and 9).

In discussing these results, we can thus conclude first that the relations of the type as given by Eqs. (4)–(6) and their consequences describe in an essentially correct way both the dependence of the glass transition temperature and the width of the glass transition temperature on cooling and heating rates. However, as well-known, while the glass transition interval is essentially determined by a relation of the type of Eq. (4), different specific definitions of the glass transition temperature are employed leading frequently to quantitatively quite different results (cf., e.g., Refs. 1, 12, 13, 18, and 19). In this way, having in mind these uncertainties, we can generalize Eq. (4)

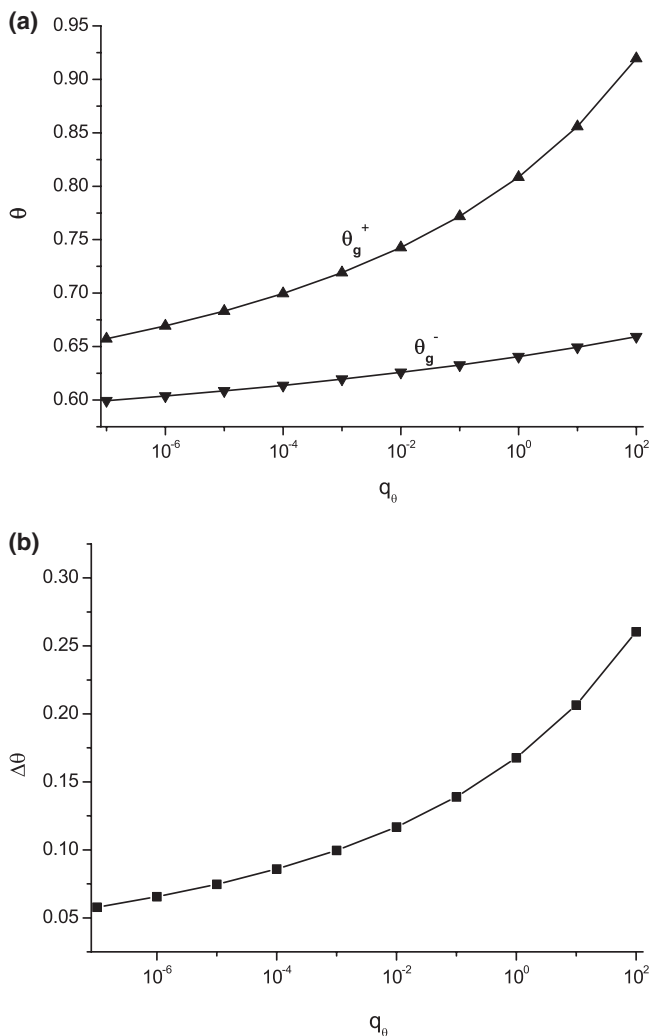


FIG. 6. Dependence of the upper and lower values and the width of the glass transition interval as obtained from numerical computations. Here the notation $\theta = T/T_m$ (T_m is the melting temperature) are employed (for the details of the computations see also Refs. 8, 9, and 14). The values of the parameters are: $T_m = 750$ K, $T_0 = T_m/2$, $B = 5T_m$.

writing it in the form

$$T_g : \tau_R \cong \tau_T \Rightarrow \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\} \Big|_{T=T_g} = \alpha^{(T_g)}, \quad (42)$$

where $\alpha^{(T_g)}$ is of the order but not necessarily equal to one. In addition, Eq. (7) is a quite reasonable but, anyway, an assumption, other assumptions may be more appropriate. In this way, applying above analytical expressions, Eqs. (4)–(6) (or its generalization Eq. (42)) to the description of experimental data or theoretical results like those discussed in the present section, a method of determination of the values of the parameters $\alpha^{(T_g)}$, $\alpha^{(+)}$ and $\alpha^{(-)}$ has to be developed which is in agreement with the method of determination of the glass transition temperature and the boundaries of the glass transition range utilized.

For example, in application to the interpretation of experimental data, this can be done as follows: Provided one has determined T_g , $T_g^{(+)}$, and $T_g^{(-)}$ for one given cooling and heating rate, then – specifying in a definite way the glass transition temperature and the boundaries of the glass transition range can be approximated also quantitatively quite well

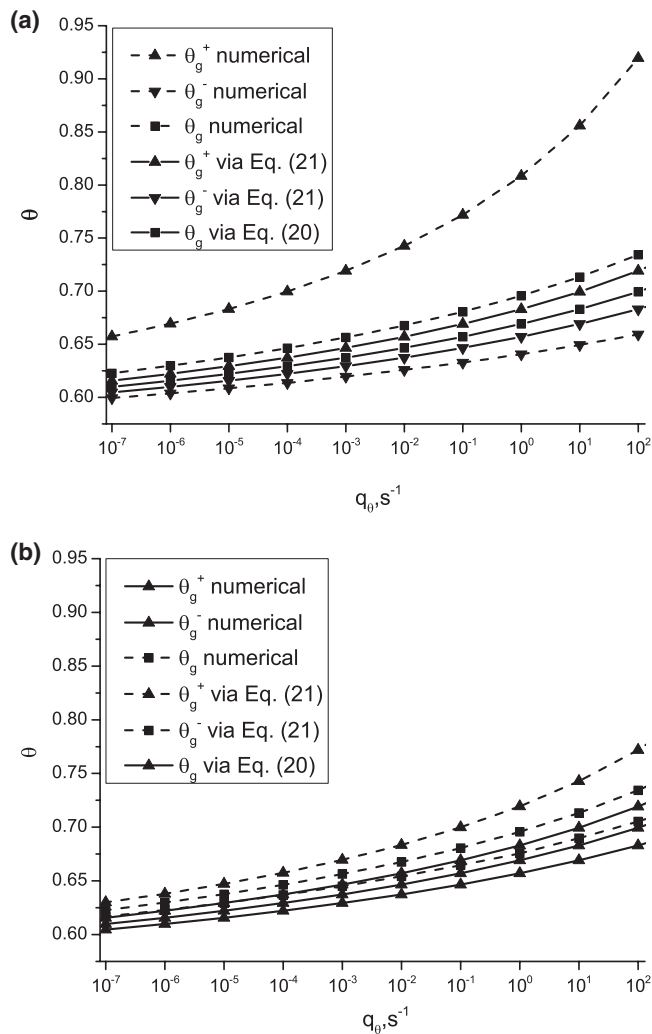


FIG. 7. Comparison of analytical relations and numerical computations: In this figure, both the first (a) and the second (b) methods of specification of the boundaries of the glass transition interval are employed and specified based on the results of the numerical computations (dashed curves). In the figure, in addition, a comparison with the analytical results based on Eqs. (4)–(6) is given (full curves).

transition interval – the values of $\alpha^{(+)}$ ($\alpha^{(+)} \cong 10^{-3}$), $\alpha^{(-)}$ ($\alpha^{(-)} \cong 0.33$), and $\alpha^{(T_g)}$ ($\alpha^{(T_g)} \cong 0.016$) can be determined comparing these results with the analytical expressions given by Eqs. (5), (6), and (42). Having obtained the respective values of these parameters, these equations can be used then as estimates of the values of T_g and the boundaries of the glass transition interval for the other values of cooling and heating rates employing the same relations. Similarly, performing numerical computations employing an appropriate model of the system under consideration, one can proceed in the same way by determining the respective parameters α based on computations for one cooling and heating rate and employing the results then for estimates of the behavior at other values of the cooling and heating rates.

One example in this respect, where such approach is realized, is demonstrated in Fig. 8. Here it is shown that with appropriately chosen values of $\alpha^{(+)}$, $\alpha^{(-)}$, and $\alpha^{(T_g)}$ the glass transition temperature and the boundaries of the glass transition range can be approximated also quantitatively quite well

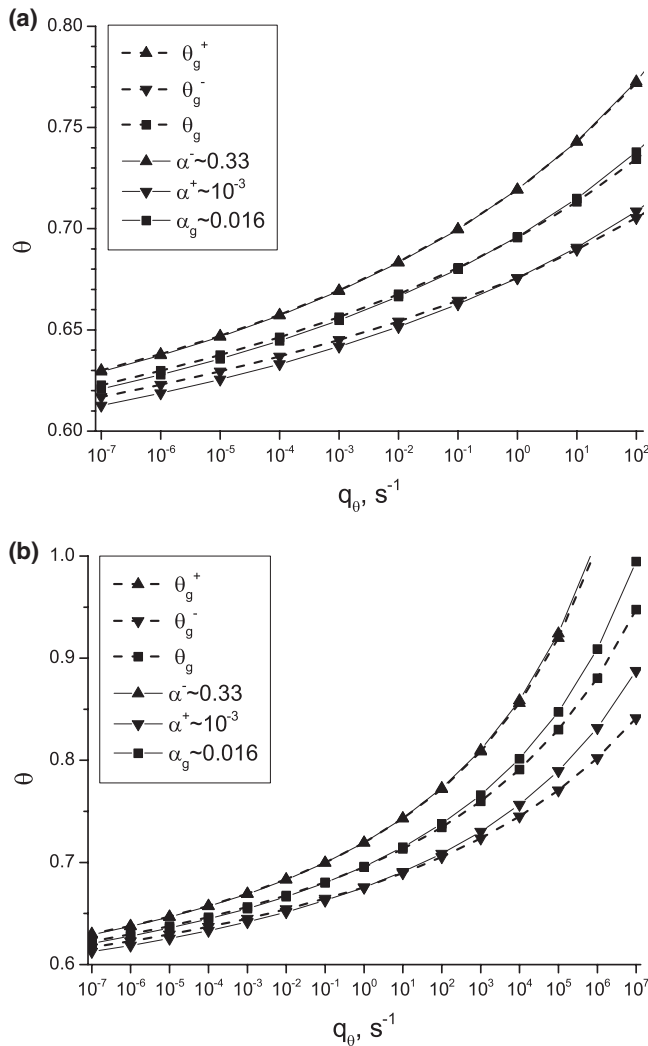


FIG. 8. Comparison of analytical relations and numerical computations: Here it is shown that with appropriately chosen values of $\alpha^{(+)}$, $\alpha^{(-)}$, and $\alpha^{(T_g)}$ (cf., Eqs. (5), (6), and (42)) the glass transition temperature and the boundaries of the glass transition range can be approximated also quantitatively correctly by varying the rate of change of temperature by more than ten decades.

by varying the rate of change of temperature by more than ten decades. Note that the relative values of $\alpha_{rel}^{(+)} = (\alpha^{(+)}/\alpha^{(T_g)}) \cong 0.05$ and $\alpha_{rel}^{(-)} = (\alpha^{(-)}/\alpha^{(T_g)}) \cong 16$ referred to the revised definition of T_g via Eq. (42) are quite similar to the original estimates of $\alpha^{(+)}$ and $\alpha^{(-)}$ as given by Eq. (7) for the original definition of T_g via Eq. (4).

IV. DETERMINATION OF THE WIDTH OF THE GLASS TRANSITION INTERVAL: AN ALTERNATIVE THERMODYNAMICALLY BASED ANALYTICAL APPROACH

A. Basic equations

In the preceding analysis, we have developed and applied two methods of determination of the boundaries and the width of the glass transition interval in dependence on cooling and heating rates. The first of them consists in the application of the basic kinetic criteria of glass-formation described by

Eqs. (4)–(7) (Sec. II) or its modification as discussed in Sec. III B. The second approach involves a numerical integration of the set of basic kinetic equations for the description of the glass transition employing an appropriate model system as described in Sec. III A. In the present section, we would like to return to a derivation of analytical estimates of the width of the glass transition interval based not directly on the kinetic criteria of glass formation but on some general relations describing the glass transition derived in the framework of the thermodynamics of irreversible processes. Of course, both methods are not independent but interrelated.

The starting point of this part of our analysis is illustrated in Fig. 1. In this figure, the entropy production is shown as a function of reduced temperature for some given (constant absolute) value of the cooling and heating rate. Since above the glass transition range, the system is found in a (meta)stable thermodynamic equilibrium, in this range the entropy production is equal to zero. Similarly, once the system is frozen-in to a glass, irreversible processes may not proceed and the entropy production is equal to zero, again. Values of the entropy production different from zero can be found consequently only in the glass transition interval. As already discussed, there exists some freedom in the definition of the glass transition temperature.^{1,12,13,18,19} In the present section, we consider mainly cooling processes and identify the glass transition temperature with the position of the maximum of entropy production. This particular definition of the temperature of glass transition employed here can be denoted as a special version of a thermodynamically based definition (cf., also Refs. 10–13). The width of the glass transition range we will estimate then by expanding the expression for the entropy production into a truncated Taylor series with respect to temperature up to second-order terms in the deviations from T_g . In a general form, we may then write

$$\begin{aligned} \frac{d_i S}{dT} &= \left(\frac{d_i S}{dT} \right) \Big|_{T=T_g} + \frac{1}{1!} \frac{d}{dT} \left(\frac{d_i S}{dT} \right) \Big|_{T=T_g} (T - T_g) \\ &+ \frac{1}{2!} \frac{d^2}{dT^2} \left(\frac{d_i S}{dT} \right) \Big|_{T=T_g} (T - T_g)^2. \end{aligned} \quad (43)$$

The first-order derivative of the entropy production is equal to zero at T_g and the second-order derivative is by necessity negative (as noted, we identify T_g with the maximum of the entropy production). The half-width of the glass transition interval is determined then by the condition $(d_i S/dT) = 0$ and for the width of the glass transition range we obtain the general result

$$T_g^{(+)} - T_g^{(-)} = 2 \sqrt{\frac{\left(\frac{d_i S}{dT} \right) \Big|_{T=T_g}}{-\frac{1}{2} \frac{d^2}{dT^2} \left(\frac{d_i S}{dT} \right) \Big|_{T=T_g}}}. \quad (44)$$

It follows that the width of the glass transition region is proportional to the square root of the entropy production at T_g . In the subsequent analysis in this section, we would like to derive some further conclusions.

Restricting the analysis, again, to glass-forming systems which can be described by one additional structural order

parameter, the entropy production due to irreversible processes in the system may be expressed as^{1,2,14,20,21}

$$\frac{d_i S}{dT} = \left(\frac{A}{T}\right) \frac{d\xi}{dT}. \quad (45)$$

Here the change of structural order parameter is described for the processes considered by us by

$$\frac{d\xi}{dT} = -\frac{1}{q\tau_R}(\xi - \xi_e), \quad q = \frac{dT}{dt}, \quad (46)$$

again, where the affinity is given, approximately, by

$$A = -G_e^{(2)}(\xi - \xi_e). \quad (47)$$

For the model system, employed already in Sec. III, we can write approximately

$$A \cong -\frac{RT}{\xi_e}(\xi - \xi_e). \quad (48)$$

We will utilize here this model as well having shown its ability to describe a large variety of glass-forming systems in an, at least, qualitatively widely correct way.^{1,2}

These general thermodynamic relations can be supplemented by two relations which follow from the general kinetic criterion for glass transition. In the glass transition range, the relation Eq. (4) has to be fulfilled. Multiplying this relation by temperature, T , and taking the derivative with respect to temperature, we obtain

$$\left|q \frac{d\tau}{dT}\right|_{T=T_g} \cong 1. \quad (49)$$

This relation has been derived for another model system for the first time by Volkenstein and Ptizyn.^{22,23} In addition, Eqs. (2)–(4) yield

$$\left\{\frac{T}{(\xi - \xi_e)} \frac{d\xi}{dT}\right\}_{T=T_g} \cong -1. \quad (50)$$

B. Computations

With above relations, we may write

$$\frac{d_i S}{dT} = \frac{R}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e}. \quad (51)$$

The extremums of the entropy production obey the relations

$$\begin{aligned} \frac{d}{dT} \frac{d_i S}{dT} = R \left\{ \left[-\frac{1}{(q\tau_R)^2} \frac{d}{dT} (q\tau_R) \right] \frac{(\xi - \xi_e)^2}{\xi_e} \right. \\ \left. + \frac{1}{q\tau_R} \frac{d}{dT} \left[\frac{(\xi - \xi_e)^2}{\xi_e} \right] \right\} = 0, \end{aligned} \quad (52)$$

$$\frac{d}{dT} \frac{d_i S}{dT} = \frac{d_i S}{dT} \left\{ \left[-\frac{d}{dT} \ln(q\tau_R) \right] + \frac{d}{dT} \ln \left[\frac{(\xi - \xi_e)^2}{\xi_e} \right] \right\} = 0, \quad (53)$$

or, equivalently,

$$\frac{d}{dT} \frac{d_i S}{dT} = \frac{d_i S}{dT} \left\{ \frac{d}{dT} \left[\ln \left(\frac{1}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e} \right) \right] \right\} = 0. \quad (54)$$

The extremums are characterized, consequently, by two different possible relations, by either

$$\frac{d_i S}{dT} = 0 \quad (55)$$

or

$$\frac{d}{dT} \left[\left(\frac{1}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e} \right) \right]_{T=T_g} = 0. \quad (56)$$

The latter relation can be written also in the form

$$\frac{d}{dT} \ln(q\tau_R) = \frac{d}{dT} \ln \left[\frac{(\xi - \xi_e)^2}{\xi_e} \right]. \quad (57)$$

With the Volkenstein-Ptizyn relation, Eq. (49), we obtain

$$q\tau_R \cong \left\{ \frac{d}{dT} \left[\ln \left(\frac{(\xi - \xi_e)^2}{\xi_e} \right) \right] \right\}^{-1} \quad (58)$$

for states in the vicinity of T_g . Comparing this result with the basic kinetic criterion for the determination of the glass transition temperature, Eq. (4), we get

$$T_g \cong \left\{ \frac{d}{dT} \left[\ln \left(\frac{(\xi - \xi_e)^2}{\xi_e} \right) \right] \right\}^{-1}. \quad (59)$$

The second-order derivatives of the entropy production with respect to temperature can be written according to Eq. (54) as

$$\begin{aligned} \frac{d^2}{dT^2} \frac{d_i S}{dT} = \frac{d}{dT} \left(\frac{d_i S}{dT} \right) \left\{ \frac{d}{dT} \left[\ln \left(\frac{1}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e} \right) \right] \right\} \\ + \frac{d_i S}{dT} \left\{ \frac{d^2}{dT^2} \left[\ln \left(\frac{1}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e} \right) \right] \right\}. \end{aligned} \quad (60)$$

The first term on the right hand side of this equation is equal to zero at T_g and the second term is by necessity negative (maximum of the entropy production). By substitution of Eq. (60) into Eq. (44), we get for the width of the glass transition interval the relation

$$T_g^{(+)} - T_g^{(-)} = 2 \sqrt{\frac{1}{-\frac{1}{2} \frac{d^2}{dT^2} \left[\ln \left(\frac{1}{q\tau_R} \frac{(\xi - \xi_e)^2}{\xi_e} \right) \right]_{T=T_g}}}. \quad (61)$$

This relation can be directly employed for the computation of the glass transition range knowing the temperature dependencies of ξ , ξ_e , and τ_R .

V. DISCUSSION

In the present analysis, we derived general relations specifying the boundaries and the width of the glass transition interval in cooling and heating. It was supposed in the analysis that the cooling and heating rates are constant and have the same absolute values in cooling and heating and that the relaxation time depends only weakly on the structural order parameter so that such dependence can be neglected. The general relations, Eqs. (4), (5), and (6) retain their validity, of course, also when these restrictions are not imposed. However, in such more general cases, the boundaries of the glass

transition range and the glass transition temperature will be, in general, different for cooling and heating.

As already mentioned, similar considerations can be applied when the glass transition is realized by a change of other control parameters, for example, by an increase of pressure. In addition, the method can be employed in a somewhat modified form also to dynamic glass transitions if the state of the system at given pressure and temperature is changed by some external perturbations with a characteristic angular frequency, ω .⁴ In such cases, the characteristic time of change of the external control parameter, τ_D , is given by $\tau_D \cong 1/\omega$ resulting in (Ref. 3),

$$\omega_g : \tau_D \cong \tau_R \Rightarrow \omega\tau_R|_{\omega=\omega_g} \cong 1 \quad (62)$$

as the relation for the determination of the value of the angular frequency, at which the dynamic glass transition takes place. Performing the experiments at different temperatures, one can easily arrive then at a relation connecting the value of ω at the dynamic glass transition and the current value of temperature, T_g . Assuming the Arrhenius law for the description of relaxation, Eq. (8), we arrive in this simple case at a relation of the form as derived first by Bartenev (cf., Ref. 4),

$$\frac{A}{T_g} = -(\ln \tau_0 + \ln \omega). \quad (63)$$

On the other hand, for any values of pressure and temperature of the undisturbed state, we can pose the question of the width of the interval of ω -values, where the response of the system to external perturbations is qualitatively changed. Similarly to Eqs. (5) and (6), we may then write

$$\omega_g^{(-)} : \tau_D \cong \alpha^{(-)}\tau_R \Rightarrow \omega_g^{(-)}\tau_R(T_g) \cong \alpha^{(-)} \ll 1, \quad (64)$$

$$\omega_g^{(+)} : \tau_D \cong \alpha^{(+)}\tau_R \Rightarrow \omega_g^{(+)}\tau_R(T_g) \cong \alpha^{(+)} \gg 1. \quad (65)$$

As first estimates of the values of $\alpha^{(+)}$ and $\alpha^{(-)}$ we could employ again Eq. (7). Equations (62)–(65) then yield

$$\omega_g^{(+)} - \omega_g^{(-)} \cong \alpha^{(+)}\omega_g \quad (66)$$

or, for Arrhenius relaxation,

$$\ln(\omega_g^{(+)} - \omega_g^{(-)}) \cong \ln\left(\frac{\alpha^{(+)}}{\tau_0}\right) - \frac{A}{T_g}. \quad (67)$$

In the case, relaxation is described by the VFT equation, we would get instead the slightly modified relation

$$\ln(\omega_g^{(+)} - \omega_g^{(-)}) \cong \ln\left(\frac{\alpha^{(+)}}{\tau_0}\right) - \frac{B}{T_g - T_0}. \quad (68)$$

A detailed comparison of latter results with experimental studies is in preparation.

ACKNOWLEDGMENTS

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