



ELSEVIER

Thermochimica Acta 280/281 (1996) 363–382

thermochimica
acta

Kinetics of structural relaxation of glass-forming melts¹

I. Avramov

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Abstract

This is a review of current knowledge on the kinetics of relaxation of glass-forming melts. The kinetics of the relaxation process is of prime importance for the properties of glasses. A number of approaches describing the structural relaxation of glasses are discussed. The aim is to predict the form of the relaxation function and the temperature dependence of the characteristic time for structural relaxation τ_r .

Important information on the relaxation behaviour of glasses can be obtained by following the dependence of the glass transition temperature T_g on the heating rate and the dependence of T_f on the cooling rate.

Keywords: Glass; Kinetics; Relaxation; Structure

1. Introduction

The study of the relationship between the equilibrium and non-equilibrium properties of systems is one of the fascinating problems of contemporary science. The present review summarizes the results of theory and experiment on the relaxation of glasses.

When a melt is cooled through the glass transition region, a non-equilibrium vitreous state is obtained. While every equilibrium system can be determined by a set of intensive thermodynamic parameters, like pressure P and temperature T , at least one additional parameter is needed for the complete description of a non-equilibrium system. For that reason, Tool and Eichlin [1] introduced the so called “fictive” or “structural” temperature, T_f . Generally, T_f is the temperature at which the fixed structure would be in equilibrium. The problem is that a system with a given structure could manifest different values of T_f when different properties are investigated [2]. A good illustration of this is the experiment of Ritland [3] who found that two samples with equal structural temperature with respect to refractive index could have different

¹ Dedicated to Professor Hiroshi Suga.

electrical conductivities if the thermal paths of arriving at the given state were different. More than one fictive temperature is needed in order to describe memory effects. The relaxation of many properties of glasses has been investigated so far. This includes the time dependences of viscosity, refraction indices, enthalpy and density, and the study of mechanical relaxation and neutron scattering, etc.

2. Models of relaxation kinetics

Structural relaxation is a process of establishing the equilibrium state. The time scale of this process is determined by the relaxation time τ_r . The system that is examined for a time much longer than τ_r is seen to be in equilibrium. However, when the observation time is much shorter than the relaxation time, we see a snap-shot of a frozen-in non-equilibrium system. A number of approaches describing the structural relaxation of glasses are known. The aim of the existing theories is to predict the form of the relaxation function Φ_r , and the temperature dependence of the characteristic time for structural relaxation, τ_r . The response function Φ_1 of a conventional Debye relaxation [4] of a spherical molecule in a viscous medium

$$\Phi_1 = r(t)/r_{in} = \exp(-t/\tau_e) \quad (1)$$

is characterized by a single relaxation time τ_e and by a deviation r of a given property from the equilibrium value. Hereafter, r is considered as the relative deviation of the structural temperature T_f from the actual temperature T of the system

$$r = \frac{T_f - T}{T} \quad (2)$$

Eq. (1) is the solution of a single linear differential equation

$$\dot{r} \equiv dr/dt = -r/\tau_e \quad (3)$$

which, in terms of linear non-equilibrium thermodynamics, controls the relaxation process. Eq. (1) is also known as Maxwell's law, which follows from the assumption that a given property r changes towards equilibrium as a first-order chemical reaction.

2.1. Stretched exponential

Kohlrausch, some 150 years ago [5], first noticed that Eq. (1) does not properly describe the relaxation kinetics of glasses. He [5] and later Williams and Watts and coworkers [6,7] assumed that in complex systems the response function Φ_β is a stretched exponential

$$\Phi_\beta = r(t)/r_{in} = \exp(-(t/\tau_e)^\beta), \quad 0 < \beta < 1 \quad (4)$$

Following the idea of Rendell and Ngai [8], one can derive Eq. (4) by replacing τ_e with a time-dependent function

$$\tau(t) = \tau(0)t^{1-\beta}, \quad 0 < \beta \quad (5)$$

where $1 - \beta$ plays the role of the shift factor introduced by Struik [9]

$$1 - \beta = \frac{d \ln \tau}{d \ln t} \quad (6)$$

Note that $\tau(t)$ increases with time for $\beta < 1$ and decreases for $\beta > 1$. Experimentally, when a system at equilibrium undergoes an instantaneous jump to a lower temperature, the relaxation is accompanied by an increase in $\tau(t)$, and vice versa; $\tau(t)$ is a decreasing time function for a temperature jump upwards. When a system is investigated near equilibrium, a Debye relaxation (Eq. (1)) is usually found, i.e. $\beta = 1$ and $\tau(0) = \tau_c$. Evidently, in Eq. (4), τ_c is given by

$$\tau_c = (\tau(0)\beta)^{1/\beta} \quad (7)$$

2.2. Spectra of times

A stretched exponential can be obtained within the framework of a model recently developed in a series of papers [10–17]. It is based on a fundamental postulate that structural recovery involves a distribution of retardation (or relaxation) times. In this way Eq. (4) emerges naturally from the theory of hierarchically constrained dynamics [18].

There are several new and very promising approaches which, however, are very complicated and need a lot of further work. It is worth mentioning the paper of Stillinger [19] in which the basic idea of a “basin” model is given. According to this, potential energy basins are formed and the relaxation process is controlled by the kinetics of inter-basin transition.

As a matter of fact, it is assumed in a non-explicit form in all these models [10–16] that instead of Eq. (3) there is a set of independent differential equations

$$\left\{ \begin{array}{l} dr_1/dt = -r_1/\tau_1 \\ dr_2/dt = -r_2/\tau_2 \\ \dots\dots\dots \\ dr_i/dt = -r_i/\tau_i \end{array} \right. \quad (8)$$

Each r_i has a given contribution g_i to the overall relaxation process

$$r = \langle r \rangle = \sum g_i r_i \quad (9)$$

In this way the response function is represented by a sum of exponential terms

$$\Phi_\beta = \sum g_i \exp\left(-\frac{t}{\tau_i}\right) \quad (10)$$

where τ_i are independent relaxation times.

Moynihan et al. [20] and Lindsey and Paterson [21] have tried to solve the non-exponential relaxation function given by Eq. (4) as a spectrum of relaxation times, Eq. (10). Simple Fourier transform of the decay function of Eq. (4) was not found except

for $\beta = 1$ and for $\beta = 0.5$. Nevertheless, in Ref. [20], it was shown that Eq. (10) can be approximated by Eq. (4) for $0 < \beta < 1$. There is a strong relationship between the variance in $\ln(\tau/\tau_e)$ and β .

$$\text{Var} \ln(\tau/\tau_e) \equiv \langle \ln^2(\tau/\tau_e) \rangle - \langle \ln(\tau/\tau_e) \rangle^2 \quad (11)$$

This is illustrated in Fig. 1 where we plot data from Ref. [20] of $\text{Var} \ln(\tau/\tau_e)$ against β . The approximation that we propose is given as a solid line

$$\text{Var} \ln(\tau/\tau_e) = 100 \times \exp(-6\beta) \quad 0.3 < \beta < 1 \quad (12)$$

It is clear that τ_e is a mean effective value and does not imply that there is a single relaxation time. Fitting experimental data to the Kohlrausch law, Dixon and Nagel [22] found that the relaxation widths are independent of temperature in the vicinity of the glass transition interval.

Generally speaking, three different schemes could control the relaxation. The first is the assumption [10,16,20] that the process goes on as a number of more or less independent acts, each being controlled by a particular characteristic time. Eq. (8) reflects this model. However, it can be assumed [23] that one and the same building unit (for example a segment of a macromolecular chain or SiO_2 tetrahedra in the continuous network oxide glasses, etc.) can occupy different states (different energy,

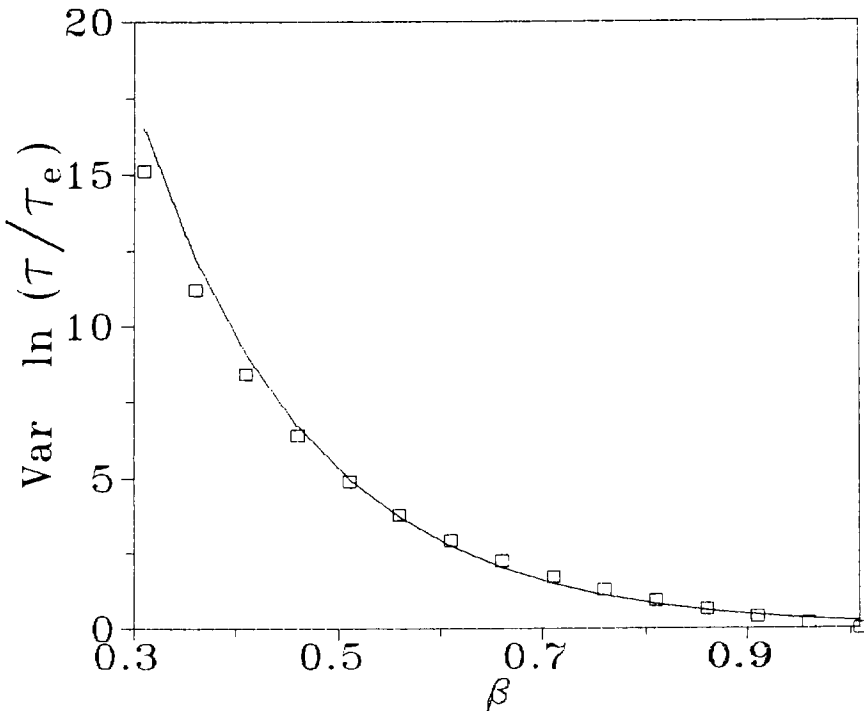
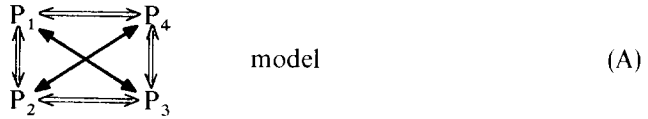
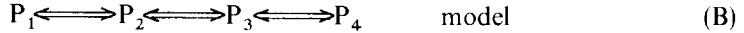


Fig. 1. Dependence of $\text{Var} \ln(\tau/\tau_e)$ on β : \square , data according to Ref. [20]; solid line, proposed approximation.

different volume, etc.) If the concentration of a given state i is P_i , and the number of states is N then the process of relaxation proceeds according to one of the following schemes [23], given schematically here for $N = 4$:



or



According to model (A), every building unit could change from state i to any other state within the limits between 1 and N . According to the model (B), there is a linear chain of possible reactions so that the building unit can go from state i to state $i \pm 1$ only. The most important difference with the model given by Eq. (8) is that (A) and (B) determine the equilibrium values P_i^c through the rate parameter W_{ik} with which a building unit at a state i changes to a state k

$$P_i^c W_{ik} = P_k^c W_{ki} \quad (13)$$

The master equation of the relaxation is

$$\frac{dP_i}{dt} = \sum_{k=1}^N P_k L_{ki} \quad (14)$$

which is to be solved together with the normalization condition

$$\sum_{k=1}^N P_k = 1 \quad (15)$$

In Eq. (13), the rate parameters L_{ki} depend on the frequency of escape W_i in the following way

For the model (A)

$$L_{ki} = \begin{cases} W_k & , \quad i \neq k \\ -(N-1)W_k & , \quad i = k \end{cases} \quad (16)$$

For the model (B)

$$L_{ki} = \begin{cases} W_k & , \quad i \pm k \\ -2W_k & , \quad k = i, \quad i \neq 1, N \\ W_k & , \quad k = 1, N; \quad i = 2, n-1 \\ 0 & , \quad \text{otherwise} \end{cases} \quad (17)$$

The system of Eqs. (13,14) is solved in the form

$$P_k(t) = \sum_{k=1}^N B_i \exp(-\lambda_i t) \quad (18)$$

with coefficients λ_i being the solutions of the system

$$|L_{ij} - \delta_{ij}\lambda| = 0 \tag{19}$$

As soon as the P_i values are known, the calculation of the relaxation function Φ is trivial. The results of model (A) show [23] that for $N = 2$, a Debye law is satisfied. The situation changes as soon as N increases and three relaxation regions appear. This is illustrated in Fig. 2 where $\ln [-\log(\Phi)]$ is plotted against $\ln t$. If Eq. (4) holds, then a straight line with slope β and intercept $-\beta \ln \tau_e$ is expected. In the short-time region below the dashed line, a slope with $\beta = 1$ is observed. The second region in which $\beta = 0.5$ and $\ln \tau_e = 5$ is important. This is the time region ($0.06 < \tau_e < 6\tau_e$) at which the experimental measurements are usually carried out. So, this model leads again to the stretched exponential law.

2.3. Mode coupling

Mode coupling theory reveals the influence of the density fluctuations modes [24–26] on the relaxation process. The motion of a particle transfers some energy to be redistributed among the surrounding particles. It results in density fluctuation modes [27–30] with a wave vector q . The density correlation function $\Phi(t)$ is determined by

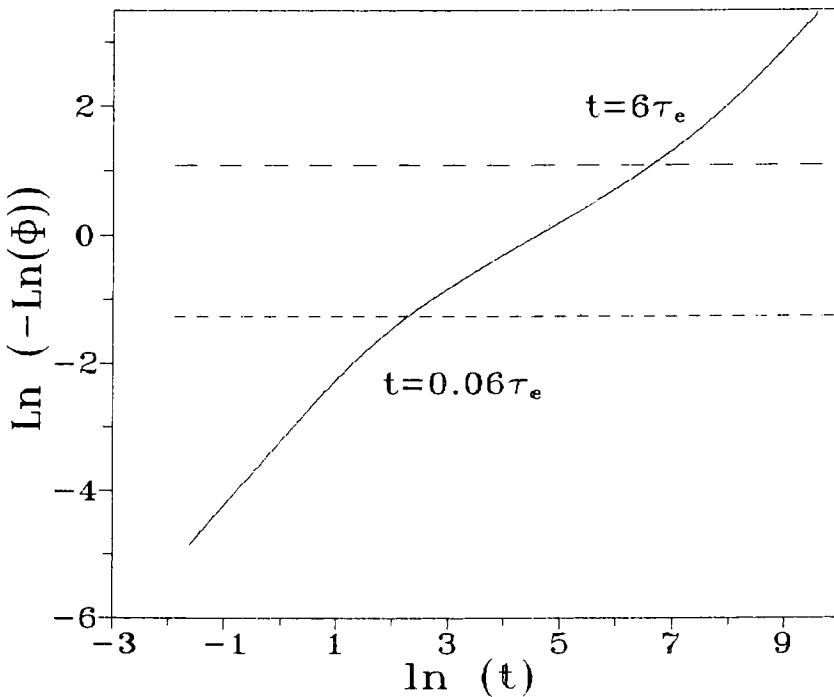


Fig. 2. $\ln [-\log(\Phi)]$ vs. $\ln t$.

the equation of motion

$$\ddot{\Phi} + (\gamma\Omega)^2 \Phi + \Omega^2 \Phi + \Omega^2 \int_0^t m(t-t')\dot{\Phi}(t')dt' = 0 \quad (20)$$

where Ω is frequency. The memory kernel $m(t)$ reflects the collective effects arising from the cooperative motion of a particle and its surrounding. Some further and non-trivial mathematical treatment of the problem are discussed in Refs. [31,32]. The theory predicts that a certain part of the relaxation proceeds according to the stretched exponential law.

By means of molecular dynamic simulation, Roe [33] investigated the short-time motion in polymer glass-forming liquid. Unlike small molecule liquids, no hopping is observed in this case. Although the mode-coupling theory predicts properly the occurrence of the glass transition, it still has long way to go in order to become applicable in a quantitative description of the relaxation when complicated temperature regimes are involved.

The simulation [1–4, 11–16] is still within the framework of linear non-equilibrium thermodynamics. However, glasses are systems very far from equilibrium. Moreover, any kinetic problem which is not properly described by Eqs. (1,3) should be treated within the framework of non-linear non-equilibrium thermodynamics. The non-linear equation of relaxation can be solved by introducing the structure-dependent relaxation time τ . Instead of Eq. (3), one has to solve the expression

$$\dot{r} = -r/\tau(r, T) \quad (21)$$

The relaxation time $\tau(r, T)$ usually depends on temperature T and structure r as [34, 35]

$$\tau = \tau_0 \exp(E(r, T)/RT) \quad (22)$$

where $E(r, T)$ is the activation energy, R is the ideal gas constant and τ_0 is a pre-exponential constant. If one assumes that at a given temperature $E(r, T)/RT$ is a linear function of the structure

$$E(r, T)/RT = E(T)/RT - pr \quad (23)$$

then Eq. (21) yields

$$\int_{pr_{in}}^{pr} \frac{e^{-pr'}}{pr'} d(pr') = -\frac{t}{\tau_c} \quad (24)$$

In this way, one derives a non-exponential relaxation. The form of Eq. (1) still holds

$$M(t) = -\frac{t}{\tau_c} \quad (25)$$

only this time one has a respond function $M(r)$ expressed in terms of an exponential integral

$$M(t) = E_i(pr_{in}) - E_i(pr) \quad (26)$$

where the exponential integral stands for

$$E_i(u) = \int_u^\infty \frac{e^{-x}}{x} dx \quad (27)$$

The $E_i(u)$ function is available in every mathematical handbook and can be represented by one of the series

$$E_i(u) = -\gamma - \ln u + \left(\frac{u}{1.1!} - \frac{u^2}{2.2!} + \frac{u^3}{3.3!} - \dots \right) \quad (28a)$$

or

$$E_i(u) \sim \frac{e^{-u}}{u} \left(1 - \frac{1!}{u} + \frac{2!}{u^2} - \dots \right) \quad (28b)$$

3. Models of the time τ of structural relaxation

The time for structural rearrangements of any complex system is related to some activation energy barrier according to

$$\tau = \tau_0 \exp \left(\frac{E(T, T_f)}{RT} \right) \quad (29)$$

where the pre-exponential constant τ_0 is between 10^{-10} and 10^{-12} s, while the activation energy $E(T, T_f)$ depends on both T and T_f . Note that the relaxation proceeds as a number of more or less independent processes, each being controlled by a particular characteristic time.

It is quite a common assumption that the structural relaxation and the viscous flow are connected by one and the same process of rearrangement of building units of the system. If so, then these two processes will be controlled by one and the same activation energy. In which case, the average time τ_r of relaxation is the time of jump of a building unit (hereafter to be referred to as a molecule) to a new position and is proportional to shear viscosity η

$$\tau_r = K \eta \quad (30)$$

According to Refs. [27,36,37], the relaxation modulus K is $K \approx 4 \times 10^{-10} \text{Pa}^{-1}$. Eq. (30) means that the most important part of the structural relaxation is connected with a spatial rearrangement of the building units. This assumption is not trivial. Some authors argue that the activation energy of viscous flow is determined by the energy necessary to break the entanglements between the macromolecular chains, while structural relaxation is a process of local molecular reorganization so that the activation energy is determined by the difficulties connected with the motion of segments between the entanglements. It is well known that the viscosity of most of the glass-forming melts depends in a non-Arrhenius way on temperature so that the activation energy is not a constant.

A number of models were developed to describe the temperature dependence of the viscosity of undercooled melts. The old-fashioned free volume approach [38–40] first predicted a non-Arrhenius behaviour of η vs. T dependence. According to this, the molecular mobility depends on the ratio of the occupied volume to the free volume. The results of Spaepen, Turnbull and coworkers [41–43], in which the structural relaxation of metallic glasses was investigated, are similar.

3.1. Adam and Gibbs equation

Naturally, the next logical step was to consider [44,45] the motion as a cooperative process involving a simultaneous rearrangement of a large number of molecules. For this reason, both τ and η should depend on the configurational entropy S_{conf} . The best known and often used equation is that of Adam and Gibbs [45]

$$\tau = \tau_0 \exp\left(\frac{A}{TS_{\text{conf}}}\right) \quad (31)$$

According to Scherer [36], the free volume model [40] is not able to describe properly the isostructural viscosity [46,47] of oxide glasses. Although the Adam–Gibbs model fits well a large number of glass-forming melts (see for instance Refs. [36,46,47]), it fails [48–51] for others.

3.2. Avramov and Milchev equation

It is well known that despite the differences in the structure and mechanism of molecular transport, all undercooled melts show a remarkable similarity in the temperature dependence of their shear viscosity. In our previous papers [34–36], this was accounted for within a generalized model describing phenomenologically the kinetics of molecular motion in undercooled liquids and glasses. While in an absolutely ordered system a molecule has to overcome always one and the same activation energy barrier in order to move, in amorphous systems, because of the disorder, there are a number of activation energy barriers of different height E , the appearance of each being characterized by a probability distribution function $P(E)$. The distribution is characterized by the dispersity σ and the maximal value E_{max} . The mean jump frequency is defined as

$$\langle v \rangle = \int_0^{\omega} P(E)v(E) dE \quad (32)$$

It is important to note that while $v = \tau^{-1}$

$$\langle v \rangle = \langle \tau^{-1} \rangle \neq \langle \tau \rangle^{-1}$$

The mean effective time responsible for the relaxation is

$$\tau_r = \langle v \rangle^{-1} \quad (33)$$

Eq. (24) can be solved for any special choice of $P(E)$. Earlier [34, 35, 52], we showed that the exact solution of Eq. (32) together with Eqs. (33) and (29) can be approximated as

$$\tau_r \cong \tau_0 \exp\left(-\frac{E_{\max}}{\sigma}\right) \quad (34)$$

There is [34, 35, 52] a strong relationship between the entropy S and dispersity σ of the system

$$\sigma = \sigma_g \exp\left(\frac{2(S - S_g)}{ZR}\right) \quad (35)$$

Here σ_g is the dispersity of the system at a reference state at which entropy is S_g , and Z is the degeneracy of the system, i.e. it is the number of escape channels available to each molecule. For a non-equilibrium system the entropy is given by

$$S = S_g + C_p \ln\left(\frac{T_f}{T_g}\right) + C_{gl} \ln\left(\frac{T}{T_f}\right) \quad (36)$$

where C_p and C_{gl} are the molar heat capacities of the liquid and of the glassy state. Therefore

$$\tau_r = \tau_0 \exp\left[\left(\frac{\theta}{T_f}\right)^a \left(\frac{T_f}{T}\right)^g\right] \quad (37)$$

where

$$\theta = \left(\frac{E}{\sigma_g}\right)^{1/\alpha} T_g \quad (38)$$

is the virtual temperature at which $\sigma(\theta) = E_{\max}$. Here

$$a = \frac{2C_p}{ZR} \quad (39)$$

and

$$g = a \frac{C_{gl}}{C_p} \quad (40)$$

At equilibrium, $T_f = T$, so that

$$\tau_r = \tau_0 \exp\left(\frac{\theta}{T}\right)^a \quad (41)$$

Since η is proportional to τ_r , Eq. (41) gives the temperature dependence of the viscosity. This was proven for about 40 substances [52] where an empirical relationship between θ and a was found

$$\ln \theta = 6.4 + 3.6 \frac{1}{a} \quad (42)$$

and

$$\frac{E}{\sigma_g} \approx 33 \pm 1 \quad (42a)$$

3.3. Vogel–Fulcher–Tammann equation

The empirical Vogel–Fulcher–Tammann equation predicts that the activation energy for molecular motion of a system at equilibrium ($T_f = T$) is given as

$$\frac{E(T)}{RT} = \frac{A}{T - T_0} \quad (43)$$

T_0 and A being constants. This expression is widespread and is also known (for polymers) as the Williams–Landel–Ferry equation.

3.4. Narayanaswamy model

The relaxation kinetics manifest two features: non-exponentiality and non-linearity. The former is accounted for by expressing the response function by one of the equations (4, 10, 20, 25), the latter being expressed by using for the relaxation time an expression that takes into account that it depends on T_f and T . Narayanaswamy [53] wrote the relaxation time in the following form

$$\tau_r = \tau_0 \exp\left(\frac{xh}{RT} + \frac{(1-x)h}{RT_f}\right) \quad (44)$$

where the non-linearity parameter x separates the influence of temperature from that of the fictive temperature. It should be noted that Eq. (44) predicts an Arrhenius behaviour for a system close to equilibrium. The latter contradicts most of the experimental evidence and may be one of the reasons why when using Eq. (44) one obtains physically unreasonable values for the parameters involved. Despite its empirical background, Eq. (44) is very widespread because it simplifies considerably the mathematical description of the relaxation process of glasses. The accuracy of the predicted time evolution of any property of non-equilibrium systems depends critically upon the non-linearity parameter x . This is the reason why the methods of experimental determination of x become of primary importance for the study of structural relaxation.

4. Temperature treatment

Although the exact form of the response function is still under question, the non-isothermal experimental investigation of relaxation processes is very popular. The glass transition is a kinetic phenomenon. It is a problem of the ratio between the observation time Δt and the relaxation time τ_r . Conventional cooling- or heating-rate experiments are plagued by uncertainties of how to treat a system which is in the process of falling out of equilibrium. Therefore the measuring time has an important

role. For an arbitrary thermal history, the time is linearized by replacing the t/τ fraction by the reduced time [22]

$$\xi(t) = \int_0^t \frac{dt'}{\tau(t')} \quad (45)$$

Experimentally, it was found that the structural temperature T_f that is fixed upon cooling increases with the cooling rate $q^- = -dT/dt$. In DSC instruments, a continuous temperature change is simulated by making a series of almost instantaneous temperature jumps ΔT , each followed by isothermal annealing of time $\Delta t = |\Delta T|/q$. (In particular, in some of our DSC measurements [54,55] the ΔT jump was $\Delta T = 1/30$ K). In accordance with Ritland [56] and Bartenev [57]

$$\tau_r(T = T_f) = \Delta t \quad (46)$$

or

$$q^- \tau(T = T_f) = \text{Const}_1 \quad (47)$$

If a glass with a given T_f is reheated at a rate $q^+ = dT/dt$, then at the glass transition temperature T_g the structure begins to change measurably towards equilibrium. In this case, the equation of Bartenev [57–59] and Davies and Jones [60] gives

$$q^+ \tau_r(T_g, T_f) = \text{Const}_2 \quad (47a)$$

Another definition that leads to Eq. (47) is given by Cooper [61] and Cooper and Gupta [62]

$$\frac{d\tau}{dt} = \frac{d\tau}{dT} \frac{dT}{dt} = 1 \quad (47b)$$

If one assumes that τ_r is an exponential function (see Eq. (29)) of the activation energy, the following criterion [63] can be formulated

$$1/T_f = C_2(C_1/C_2 - \ln(q^-)) \quad (48)$$

with $C_1 = C_2(\ln(c/\tau_0))$ and $C_2 = R/E(T, T_f)$. Empirically, Bartenev and Gorbatkina [63] found that $C_1/C_2 = 31$. It is of interest to note that in Eq. (47), $\ln(q^{-1}) \ll 31$ (for $q = 1 \text{ K min}^{-1}$, $\ln q^- = 0$) so that $31 C_2 \approx 1/T_f$, or taking into account Eq. (41) one obtains

$$\left(\frac{\theta}{T_f}\right)^a = \frac{E(T, T_f)}{R T_f(q=1)} = 31 \quad (49)$$

It follows that

$$\ln \theta \approx \ln T_f + \frac{3.5}{a} \quad (50)$$

Note the good agreement between Eqs. (50) and (42).

For a constant activation energy there should be a straight line in coordinates $1/T_f$ against $\ln q^-$. (It is often presented in Arrhenius coordinates, i.e. $\ln q^-$ vs. $1/T_f$.) Usually,

the relaxation of glasses is investigated in a relatively narrow temperature region, so that experimental curves resemble straight lines. For that reason, many authors assume that the activation energy is constant. Meanwhile, there are at least two independent signs that this assumption is not correct [54,64]. The first indication follows from the proportionality of τ_r and η . Since the viscosity exhibits a non-Arrhenius behaviour, the same should be assumed for the relaxation time. The second indication follows from the fact that experimentally the two curves ($\ln q^-$ vs. $1/T_f$ and $\ln q^+$ vs. $1/T_g$) have different slopes [55,65,66]. In coordinates $\ln q^-$ against $1/T_f$, the curve has a slope L_f equal to

$$L_f = -\frac{E(T, T_f = T)}{R} - \frac{1}{RT} \left[\frac{\partial}{\partial(1/T)} E(T, T_f) + \frac{\partial}{\partial(1/T_f)} E(T, T_f) \right] \quad (51)$$

or according to Eq. (49) it is equal to

$$L_f = -a T_f \left(\frac{\theta}{T_f} \right)^a = -a T_f \left(\frac{E(T = T_f)}{RT} \right) \quad (52)$$

A semi-logarithmic plot of $\ln q^+$ versus the reciprocal glass transition temperature gives a curve with a slope L_g equal to

$$-L_g = \frac{E(T, T_f = \text{const})}{R} + \frac{1}{RT} \left[\frac{\partial}{\partial(1/T)} E(T, T_f = \text{const}) \right] \quad (53)$$

or

$$L_g = -g T_g \left(\frac{\theta}{T_f} \right)^a \left(\frac{T_f}{T_g} \right)^g = -g T_g \left(\frac{E(T_g, T_f)}{R T_g} \right) \quad (53a)$$

Strictly speaking, L_g depends, through $E(T_g, T_f)$, on the structural temperature T_f that was fixed during the previous cooling. An excellent example of this is the experiments of Kasap and Yannacopoulos [67] where a parameter, which in terms of the present discussion is L_g/L_f , was investigated experimentally for As_2Se_3 samples having different T_f values. It was shown that the value of L_g/L_f decreases by about 25% for annealed samples. This corresponds to about 20 K decrease in the T_f value of annealed samples.

The comparison of L_f and L_g at a point at which $T_g = T_f$ gives

$$\Delta L \equiv L_f - L_g = -(a - g) T_f \left(\frac{E(T_f)}{R T_f} \right) = -\frac{1}{R T_g} \frac{\partial}{\partial(1/T_f)} E(T_g, T_f) \quad (54)$$

which accounts for the structural dependence of the activation energy. However, $L_g/L_f = g/a = C_{g1}/C_p$.

The results of computer modelling of relaxation are given in Fig. 3. The computational steps are as follows. We consider the change of temperature at a rate $q = dT/dt = \Delta T/\Delta t$ as a series of instantaneous temperature jumps ($\Delta T = 1$ K), followed by an isothermal annealing of duration $\Delta t = 1/q$, reproducing the desired rate of temperature change. During the annealing, the relaxation rate is given by Eq. (21). We

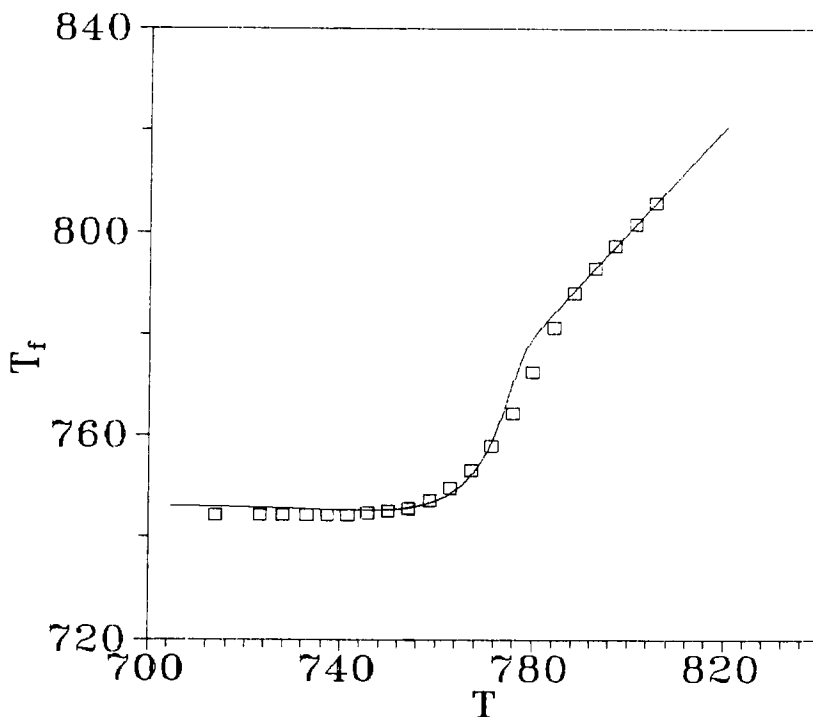


Fig. 3. Computer simulation of relaxation. Points are experimental results, from Ref. [64], on $\text{Bi}_2\text{O}_3 \cdot 3\text{GeO}_2$ (BGO 1:3) glass-forming melt cooled at $q^- = -5 \text{ K min}^{-1}$ and then heated at $q^+ = 20 \text{ K min}^{-1}$. The solid line is computed with $a = 4$, $g = 2$; $\theta = 1750 \text{ K}$ and $\tau_0 = 10^{-11} \text{ s}$ and the same thermal treatment.

integrate with a time step $t' = 10^{-4} \Delta t$ in a following loop of 10^4 steps

$$\Delta r = -\frac{r}{\tau(r, T)} t' \quad (55)$$

$$r = r + \Delta r \quad (55a)$$

$$\tau = \tau(r, T) \quad (55b)$$

If $t'/\tau(r, T) > 10^4$, then instead of running the loop it was assumed that $\Delta r = -r$; if $t'/\tau(r, T) < 1$ then instead of running the loop we simply assumed that $\Delta r = 0$. For each run the initial temperature was well above the glass transition region and the system was cooled at a steady rate q^- to a chosen temperature significantly below the glass transition interval. Then the system was heated at a rate q^+ .

Different models for $\tau(r, T)$ were used in Eq. (55b). In Fig. 3 we give the result calculated according to the model of Avramov and Milchev (Eq. (37)). The solid line is computed with $a = 4$, $g = 2$; $\theta = 1750 \text{ K}$ and $\tau_0 = 10^{-11} \text{ s}$. Points are the experimental results from Ref. [62] on $\text{Bi}_2\text{O}_3 \cdot 3\text{GeO}_2$ (BGO 1:3) glass-forming melt cooled at $q^- = -5 \text{ K min}^{-1}$ and then heated at $q^+ = 20 \text{ K min}^{-1}$.

A number of glass-forming substances were investigated by means of differential scanning calorimetry (see [10–22, 52–66]). It seems that the best way is to cycle the sample repeatedly between a temperature well below T_g and a second temperature above T_g . In one set of experiments a series of constant cooling rates could be used while the heating rate is kept constant. In another series of experiments, a constant cooling rate is followed by a range of heating rates. It must be verified that no crystallization takes place in the chosen temperature region [54,55,64–66].

The dependence of $\ln q$ vs. $10^4/T_f$ is shown in Fig. 4 for BGO glass [64]. The influence of q^+ on T_g is shown in the same figure in coordinates $\ln q$ vs. $10^4/T_g$ for samples cooled at a rate $q^- = 20 \text{ K min}^{-1}$. Solid lines are the results of computer modelling. The region of temperatures is so narrow that the experimental curves could be successfully described by the dashed straight lines. For similar reasons many authors assume that the activation energy is constant, i.e. the second term in Eq. (51) vanishes and the activation energy can be determined directly from L_f . It is readily seen that such a procedure leads to an overestimation of E by more than 100% because $L_g/L_f \approx 0.5$.

The method of Narayanaswamy [53] is very widespread, despite its empirical background, because it simplifies considerably the mathematical description of the relaxation process of glasses. The accuracy of the prediction of the time evolution of any

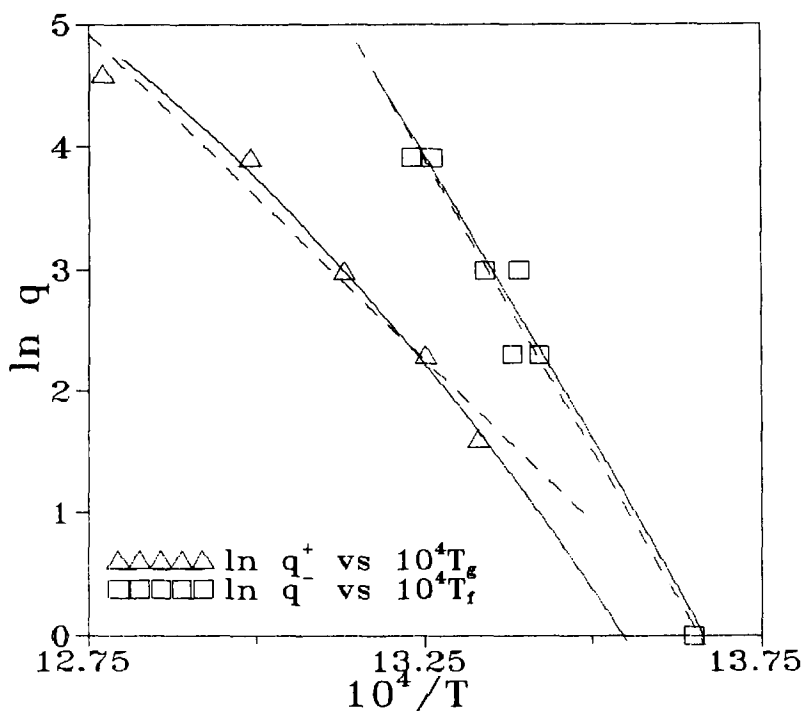


Fig. 4. Dependence of $\ln q$ vs. $10^4/T_f$ (\square) and dependence of $\ln q$ vs. $10^4/T_g$ (Δ) of $\text{Bi}_2\text{O}_3\cdot 3\text{GeO}_2$. The solid lines are computed with the same values of the parameters as in Fig. 3. The dashed lines are the best-fit straight lines.

property of non-equilibrium systems depends critically upon the utilized value of the parameter x . In a series of papers [54,55,64,66], we have shown that the non-linearity parameter x is equal to L_g/L_r . Indeed, according to Eq. (44) it follows that

$$\partial \ln (\tau(T_f = T)) / \partial (1/T) = -\Delta h/R \quad (56)$$

and

$$\partial \ln (\tau(T_f = \text{const})) / \partial (1/T) = -x \Delta h/R \quad (57)$$

It should be noted that there is an important internal contradiction in the Narayanaswamy model. It assumes a constant activation energy and, at the same time, the condition $L_g/L_r \neq 1$ is a strong indication that the activation energy is not a constant. For this reason, the L_g/L_r ratio cannot be predicted properly in the framework of this model. Moreover, in order to find a quantitative agreement between the computed curves and experimental data, one has often to use quite unreasonable values for the pre-exponential constant.

5. Frequency-dependent properties

Methods of direct measurement of the spectra of frequencies of change of under-cooled melts have recently become very important. There are measurements on mechanical and electrical relaxation [68]. Birge and Nagel [69,70] have developed a new technique for measuring the frequency dependence of the specific heat C_p , affecting a sample with small periodically varying temperature oscillations. Büchner and Korpiun [71] have shown that the photo acoustic (PA) technique can be used to determine the equilibrium specific heat in the glass transition region. They have measured the frequency-dependent effusivity of $\text{CaNO}_3 \cdot \text{KNO}_3$ glass-forming melt. Kojima [72] has applied the PA method to study the thermal relaxation in “fragile” liquids like propylene glycol and glycerol. Recently [73], we combined differential scanning calorimetry (DSC) experiments with spectral calorimetry.

According to Büchner and Korpiun [71], the PA amplitude A and phase ϕ are related to the real and imaginary parts of the square of the effusivity kC_p , through

$$A = (kC_p)_0^{1/2} [\varepsilon'(\omega) + \varepsilon''(\omega)]^{-1/4} \quad (58)$$

$$\phi = 0.5 \arctan \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \quad (59)$$

where $(kC_p)_0^{1/2}$ is the sample effusivity far above the glass transition region, k is the thermal conductivity, $\omega = 2\pi f$, $\varepsilon'(\omega) = \text{Re} \{kC_p\}$ and $\varepsilon''(\omega) = \text{Im} \{kC_p\}$. The real part of the response function is proportional to the frequency-dependent heat capacity $C_p(\omega)$, while its imaginary part accounts for the dissipative processes.

Fig. 5 shows the temperature dependence of the PA amplitude (Fig. 5a) and phase (Fig. 5b) in the glass transition region of poly(methyl methacrylate) (PMMA) for two modulation frequencies. The glass transition is accompanied by a drop in the PA

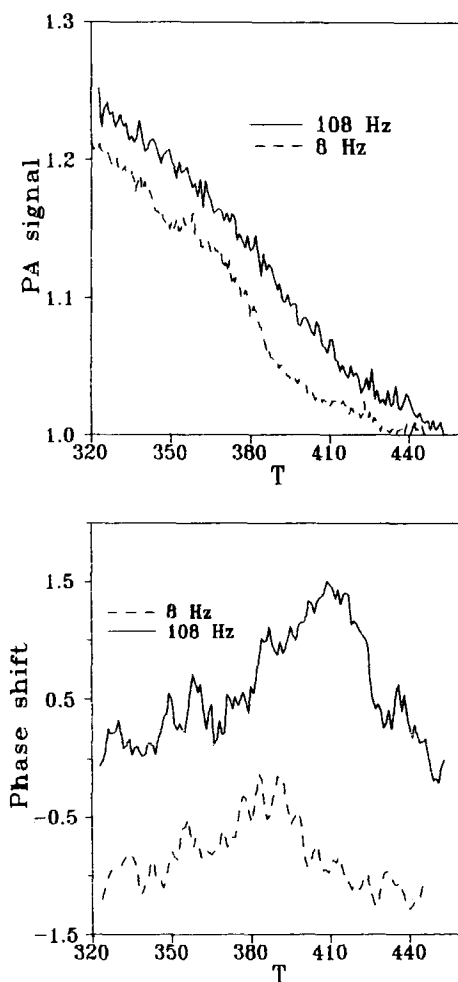


Fig. 5. The temperature dependence of the PA amplitude (a) and phase (b) of poly(methyl methacrylate) PMMA for two modulation frequencies, 8 and 108 Hz.

amplitude and by a maximum of the phase versus temperature curves (usually called the α -relaxation peak). The glass transition temperature T_g is determined from the position of the α -peak. It is readily seen that T_g shifts to higher temperatures and the α -peaks are broadened as the frequency increases. At low temperatures (340–360 K), additional small peaks are also seen. This transition is well-resolved from the α -relaxation peak at low modulation frequencies. When the frequency increases, the additional peaks move to higher temperatures faster than the α -peak. At $f = 108$ Hz, both transitions coincide. This behaviour can be associated with the secondary or β -relaxation transition [74].

6. Concluding remarks

The main advantage of non-isothermal measurements is that they allow a check of the validity of the assumption that the relaxation time of thermal relaxation is proportional to shear viscosity η . This means that the process of structural relaxation is strongly dependent on the process of molecular transport. In other words, it assumes that structural changes are possible only when molecules alter position. This assumption is not trivial. In polymers there are a number of entanglements between macromolecular chains. For that reason, some authors argue that molecular motion is controlled by the activation energy to break the entanglements, while structural relaxation is controlled by a rearrangement of segments between entanglements. The check of the assumption of proportionality between τ and η is easy when the slopes of the $\log q^-$ vs. $1/T_f$ curve and of the $\log \eta$ vs. $1/T$ curve are compared in the same temperature interval. In this way the above assumption was proved for B_2O_3 , BSC glass and $0.4Ca(NO_3)_2-0.6KNO_3$ [11,75], for $Ge_{16}Te_{84}$ alloy [76] and for some phosphate glasses [55]. Although there are some data on the kinetics of relaxation of organic polymers, the decisive test is still in the future.

A keyword reference on the word “relaxation” gives more than 2000 articles. Here only a few of them were reviewed. The author hopes that they indicate the basic ideas and problems on the topic.

References

- [1] A. Tool and C. Eichlin, *J. Am. Ceram. Soc.*, 14 (1931) 276.
- [2] R.O. Davies, G.O. Jones, *Proc. R. Soc. London, Ser. A*, 217 (1953) 26.
- [3] H.N. Ritland, *J. Am. Ceram. Soc.*, 39 (1956) 403.
- [4] P. Debye, *Polar Molecules*, Dover, New York, 1945.
- [5] R. Kohlrausch, *Ann. Phys. (Leipzig)*, 12 (1847) 393.
- [6] G. Williams and D. Watts, *Trans. Faraday Soc.*, 66 (1970) 80.
- [7] G. Williams, D. Watts, S. Dev and A. North, *Trans. Faraday Soc.*, 67 (1971) 1323.
- [8] R. Rendell and K. Ngai, in K. Ngai and G. Wright (Eds.), *Relaxation in Complex Systems*, Office of Naval Research, Arlington, VA 1084, p. 309.
- [9] L. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, Amsterdam, 1978.
- [10] I. Hodge, *J. Non-Cryst. Solids*, 160 (1994) 211.
- [11] M.A. DeBolt, A.J. Easteal, P.B. Macedo and C.T. Moynihan, *J. Am. Ceram. Soc.*, 59 (1976) 16.
- [12] A.J. Kovacs, J.J. Aklonis, J.M. Hutchinson and A.R. Ramos, *J. Polym. Sci. Polym. Phys. Ed.*, 22 (1979) 1097.
- [13] J.M. Hutchinson and J. A. Kovacs, *Polym. Eng. Sci.*, 24 (1984) 1087.
- [14] J.M. Hutchinson, J.J. Aklonis and A.J. Kovacs, *Polym. Prepr.*, 16 (1975) 94.
- [15] J.M. Hutchinson and A.J. Kovacs, *J. Polym. Sci. Polym. Phys. Ed.*, 14 (1976) 1575.
- [16] I.M. Hodge and A. Berens, *Macromolecules*, 15 (1982) 762.
- [17] S. Mazur, *J. Chem. Phys.*, 93 (1990) 3542.
- [18] R.G. Palmer, D.L. Stein, E. Abrahams and P.W. Anderson, *Phys. Rev. Lett.*, 53 (1984) 958.
- [19] F. Stillinger, *Phys. Rev.*, B41 (1990) 2409.
- [20] C. Moynihan, L. Boesh and N. Laberge, *Phys. Chem. Glasses*, 14 (1973) 122.
- [21] C. Lindsey and G. Paterson, *J. Chem. Phys.*, 73 (19) 3348.
- [22] P. Dixon and S. Nagel, *Phys. Rev. Lett.*, 61 (1988) 341.
- [23] I. Avramov and V. Tonchev, to be published.

- [24] W. Gotze and L. Sjogren, *Rep. Progr. Phys.*, 55 (1992) 241.
- [25] L. Sjogren and W. Gotze, *J. Non-Cryst. Solids*, 172–174 (1994) 7.
- [26] H. Gummins, G. Li, W. Du and J. Hernandez, *J. Non-Cryst. Solids*, 172–174 (1994) 26.
- [27] G. Scherer, *J. Non-Cryst. Solids*, 123 (1990) 75.
- [28] A. Sjolander, *Physica*, 127B (1984) 327.
- [29] U. Bengtzeliuss and A. Sjolander, *Ann. NY Acad. Sci.*, 484 (1986) 229.
- [30] T. Kirkpatrick and P. Wolynes, *Phys. Rev.*, A35 (1987) 3072.
- [31] W. Gotze, *J. Phys. Condens. Matter*, 2 (1990) 8485.
- [32] G. Li, M. Fuchs, W. Do, A. Latz, N. Tao, J. Hernandez, W. Gotze and H. Cummins, *J. Non-Cryst. Solids*, 172–174 (1994) 43.
- [33] R. Roe, *J. Non-Cryst. Solids*, 172–174 (1994) 77.
- [34] I. Avramov and A. Milchev, *J. Non-Cryst. Solids*, 104 (1988) 253.
- [35] I. Avramov, *J. Chem. Phys.*, 95 4439 (1991).
- [36] G. Scherer, *J. Am. Ceram. Soc.*, 67 (1984) 504.
- [37] O.V. Mazurin, *J. Non-Cryst. Solids*, 25 (1977) 130.
- [38] A. Batchinski, *Z. Phys. Chem. (Leipzig)*, 84 (1913) 644.
- [39] A. Doolittle, *J. Appl. Phys.*, 22 (1951) 1471.
- [40] P. Macedo and T. Litovitz, *J. Chem. Phys.*, 42 (1965) 245.
- [41] F. Spaepen, *J. Non-Cryst. Solids*, 31 (1973) 513.
- [42] M. Cohen and D. Turnbull, *J. Chem. Phys.*, 31 (1959) 1164.
- [43] F. Spaepen and G. Turnbull, *Scr. Metall.*, 8 (1974) 563.
- [44] J. Gibbs and E. DiMarzio, *J. Chem. Phys.*, 28 (1958) 373.
- [45] G. Adam and J. Gibbs, *J. Chem. Phys.*, 43 (1965) 139.
- [46] O.V. Mazurin, Yu.K. Startsev and L.N. Potselueva, *Sov. J. Phys. Chem. Glass*, 5 (1979) 66 (Engl. Transl.).
- [47] O.V. Mazurin, Yu.K. Startsev and S. Stoljar, *J. Non-Cryst. Solids*, 52 (1982) 105.
- [48] W. Laughlin and D. Uhlmann, *J. Phys. Chem.*, 76 (1972) 2317.
- [49] R. Greet and D. Turnbull, *J. Chem. Phys.*, 46 (1967) 1243.
- [50] R. Greet and D. Turnbull, *J. Chem. Phys.*, 47 (1967) 2185.
- [51] D. McCall, D. Douglas and D. Falkone, *J. Chem. Phys.*, 50 (1969) 1839.
- [52] I. Avramov, *J. Mater. Sci. Lett.*, 13 (1994) 1367.
- [53] O.S. Narayanaswamy, *J. Am. Ceram. Soc.*, 54 (1971) 491.
- [54] I. Avramov and Ts. Vassilev, *Polym. Polym. Compos.*, 2 (1994) 241.
- [55] I. Avramov, N. Avramova and I. Gutzow, *J. Non-Cryst. Solids*, 91 (1987) 386.
- [56] H.N. Ritland, *J. Am. Ceram. Soc.*, 37 (1954) 370.
- [57] G.M. Bartenev, *Structure and Mechanical Properties of Inorganic Glasses* (in Russian), Publ. Lit. po Stroitelstvu, Moscow, 1966.
- [58] G. Bartenev, *Dokl. Akad. Nauk SSSR*, 76 (1951) 227.
- [59] G. Bartenev, I. Rasumovskaya, D. Sanditov and I. Lukyanov, *J. Polym. Sci.*, A1 (1969) 2147.
- [60] R.O. Davies and G.O. Jones, *Irreversible Approach to Equilibrium in Glasses*, *Proc. R. Soc. London, Ser. A*, 217 (1953) 26.
- [61] A. Cooper, *Glastech. Ber.*, 56K (1983) 1160.
- [62] A. Cooper and P. Gupta, *Phys. Chem. Glasses*, 23 (1982) 44.
- [63] G. Bartenev and Y. Gorbatkina, *Russ. J. Phys. Chem.*, 29 (1955) 1486.
- [64] I. Avramov, G. Gnappi and A. Montenero, *Phys. Chem. Glasses*, 33 (1992) 140.
- [65] I. Avramov, N. Avramova and S. Fakirov, *J. Polym. Sci B*, 27 (1989) 2419.
- [66] I. Avramov, N. Avramova and S. Fakirov, *Makromol. Chem. Rapid Commun.*, 11 (1990) 135.
- [67] S.O. Kasap and S. Yannacopoulos, *Phys. Chem. Glasses*, 31 (1990) 71.
- [68] J. Wong and C.A. Angell, *Glass Structure by Spectroscopy*, Marcell Dekker, New York, 1976, Chap. 11.
- [69] N.O. Birge and S.R. Nagel, *Phys. Rev. Lett.*, 54 (1985) 2674.
- [70] N.O. Birge, *Phys. Rev. B*, 34 (1986) 1631.
- [71] B. Büchner and P. Korpiun, *Appl. Phys. B*, 41 (1987) 29.
- [72] S. Kojima, in O.I. Leroy and M.H. Breazeale (Eds.), *Physical Acoustics*, Plenum Press, New York, 1991.

- [73] Ts. Vassilev, I. Avramov, Ts. Velinov and S. Surnev, *Solid State Commun.*, 91 (1994) 49.
- [74] J. Heijboer, *Int. J. Polym. Mater.*, 6 (1977) 11.
- [75] C. Moynihan, A. Eastal and M. DeBolt, *J. Am. Ceram. Soc.*, 54 (1971) 491.
- [76] C. Bergman, I. Avramov, C. Zahra and J-K. Mathieu, *J. Non-Cryst. Solids*, 70 (1985) 367.