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Rate-determining factors for structural relaxation in non-crystalline materials I. Stabilization period of isothermal volume relaxation

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Abstract

The isothermal volume relaxation rate in non-crystalline materials is analyzed for the Tool–Naraynaswamy–Moynihan phenomenological model. It is demonstrated that the mathematical analysis of the inflectional slope of isothermal relaxation curve yields in a simple equation relating parameters of non-exponentiality, non-linearity, effective activation energy and the stabilization period of isothermal volume relaxation response. It can be expected that in non-crystalline materials with comparable non-linearity the temperature dependence of the stabilization period is controlled by the parameter $\theta = \Delta h^*/RT_g^2$. Materials with higher value of parameter θ (organic polymers) exhibit relatively low relaxation rate. In contrast, higher relaxation rate is expected for materials with low value of θ (inorganic glasses). The applicability of this approach for analysis of previously reported isothermal volume relaxation data of polyvinylacetate (PVA) and arsenic sulfide glass (As_2S_3) is discussed. © 1998 Elsevier Science B.V.

Keywords: Structural relaxation; Dilatometry; Glass

1. Introduction

Non-crystalline materials below their glass transition temperature (T_g) exist in a non-equilibrium state characterized by excess thermodynamic quantities (volume, enthalpy, etc.). Such systems appear to be unstable and the material undergoes a relaxation process which attempts to reduce these excess quantities towards equilibrium. It is well established that such structural relaxation process is markedly non-linear and non-exponential [1–3]. Non-linearity is indicated by the asymmetry of relaxation response following positive or negative departures from equilibrium. It is observed for temperature changes greater than about 2 K from equilibrium. Non-exponentiality is demonstrated by well known memory effect, in which relaxation from some initial state depends on how that state was reached.

The pioneering work of Tool [1] and Kovacs [2,3] established a basis for further development of phenomenological models [4,5] of the relaxation behavior of non-crystalline materials below the glass transition temperature T_g. These phenomenologies give quite good description of volume and enthalpy relaxation near equilibrium and they provide a valuable insight into the physical origin of non-linearity. Some pro-

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blems arise when the relaxation occur far from equilibrium state and there are still may unanswered questions in this respect [6].

It is usually assumed that the isothermal volume relaxation measured by dilatometry after simple quench of a material from equilibrium does not provide a very critical examination of the relaxation process and that both non-linearity and non-exponentiality effects can hardly be separated [7]. Nevertheless, we believe that the data obtained from these experiments have at least the same relevance and the information content as data from widely used calorimetric experiments. The aim of this paper is to analyze the rate limiting factors for the relaxation response of such experiments within the most frequently used phenomenological model. It is shown that mathematical analysis of the inflectional slope of the relaxation curve yields in a simple equation which can be used (under certain circumstances) for prediction of the temperature dependence of the isothermal volume relaxation rate in different non-crystalline materials.

2. Theoretical aspects

2.1. Isothermal volume relaxation

If an non-crystalline material is equilibrated at temperature T_0 (usually near T_g) and then suddenly cooled to temperature T, the volume will change as shown in Fig. 1(a). During the rapid change in temperature the vibrational response causes an instantaneous change of volume corresponding to $\alpha_g(T-T_0)$ because the structure does not change. Structural changes then take place during the isothermal hold at T and therefore the volume will change gradually toward its equilibrium value at this temperature (stabilized glass).

Isothermal volume relaxation is usually described [2,3] by the relative departure δ of actual volume V from equilibrium volume V_∞, and defined as

$$\delta = \frac{V - V_\infty}{V_\infty} \tag{1}$$

Initial departure from equilibrium δ_i is related to the magnitude of temperature jump $\Delta T = T_0 - T$ and defined as

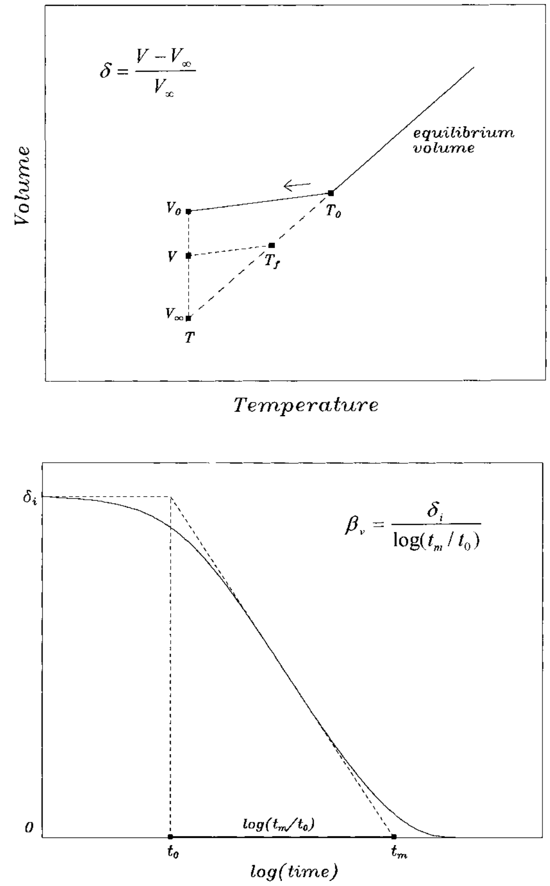

Fig. 1. (a) Schematic illustration of the volumetric changes of a stabilized non-crystalline material subjected to a temperature jump from temperature T_0 to T. During an isothermal hold at T the volume relaxes from the initial value V_0 toward its equilibrium value V_∞. (b) Isothermal volume relaxation curve corresponding to the thermal history depicted above.

$$\delta_i = \Delta\alpha \cdot \Delta T \tag{2}$$

where $\Delta\alpha$ is the difference between the volume thermal expansion coefficient of equilibrium undercooled liquid and asymptotic volume thermal expansion coefficient of glass.

Time dependence of the δ function is usually plotted on logarithmic time scale as shown in Fig. 1(b). Broken line corresponds to the inflectional tangent, which intersects ordinates at one and zero corresponding to values of times t_0 and t_m, respectively. The logarithmic difference of these two values $\log(t_m/t_0)$ defines the stabilization period of volume relaxation at a given temperature and it is inversely proportional to volume relaxation rate per decade of time. The volume relaxation rate depends on thermal history of non-crystalline material. If the temperature T_0 is relatively high then the relaxation response will be faster because corresponding structure of material is more open and the atoms and molecular clusters have more mobility than those corresponding to lower temperature equilibrium structure. During the isothermal hold the structure becomes more compact and consequently it relaxes more slowly than immediately after temperature jump. This self delaying process could be explained by implicit dependence of relaxation time upon actual structure of glass (non-linearity) and by distribution of relaxation times (non-exponentiality). This behavior simply follow from the requirement that structural relaxation involve cooperative movement which is consistent with the qualitative similarity observed in the relaxation kinetics of different glass forming systems [8].

2.2. Phenomenological description of the relaxation process

There are several phenomenological models that have been proposed for the description of the relaxation process. Any successful model must account for non-linear and non-exponential behavior mentioned above. The first important step in the development of these models was made by Tool [1], who recognized that the isothermal relaxation, following a temperature jump from an initial equilibrium state could not be described by a kinetic equation in which the structural relaxation time τ depended only upon the temperature T. He proposed that τ depended in addition upon the instantaneous structure of a glass during the relaxation, and he characterized this structure by means of the fictive temperature T_f defined as the temperature at which the specimen volume would be equal to that of the equilibrium. This dual dependence of τ on both T and T_f is refered to as the non-linearity which implies that the kinetics of isothermal relaxation do not scale linearly with the departure from the equilibrium.

A generalized expression of this dual dependence of τ upon temperature and the structure is often refereed to as Tool–Narayanaswamy–Moynihan (TNM) equation [1,4,9]:

$$\tau = A \cdot \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{3}$$

Eq. (3) introduces three constant parameters: the non-linearity parameter x ($0<x\leq 1$), the effective activation energy Δh^* and the pre-exponential factor A. According to Narayanaswamy [4], linearity can be restored using the reduced time defined by

$$\xi = \int_0^t \frac{dt}{\tau(T,t)} \tag{4}$$

If a glass is equilibrated at temperature T_0 and then subjected to sudden temperature change to temperature T (i.e. temperature jump ΔT) then the fictive temperature is expressed as

$$T_f = T_0 - \left[1 - \frac{\delta(\xi)}{\delta_i}\right] \cdot \Delta T \tag{5}$$

Therefore, the fictive temperature is equal to T_0 immediately after the temperature jump and during the isothermal relaxation it gradually changes towards T (see Fig. 1(a)) as expressed by Eq. (5).

The non-exponentiality may be introduced into Eq. (5) either by means of a stretched exponential function [6,8–10]:

$$\delta(\xi) = \delta_i \exp(-\xi^\beta) \tag{6}$$

where the parameter β is inversely proportional to the width of a corresponding continuous distribution of relaxation times ($0<\beta\leq 1$), or by means of a discrete distribution as suggested e.g. in the KAHR model [5]. In both cases, it is assumed that the distribution of relaxation times exhibit thermorheological simplicity, i.e. the shape of the distribution is independent of temperature.

The Eqs. (3)–(6) are sufficient to describe quantitatively the response (volume, enthalpy, etc.) of a glass to isothermal treatment below T_g. In practice, they must be solved numerically. This solution involves numerical evaluation of reduced time integral defined by Eq. (4) which is accomplished by dividing total aging time into sufficient number of subintervals and calculating corresponding change of T_f at the end of each subinterval as suggested by Hodge and Berens

[11] and Scherer [10]. The Eq. (5) then can be expressed as

$$T_{\mathrm{f},n} = T_0 - \left(1 - \exp\left[-\left(\sum_{j=1}^{n} \frac{\Delta t_j}{\tau_j}\right)^{\beta}\right]\right) \cdot \Delta T \tag{7}$$

where τ_j is given by

$$\tau_j = A \cdot \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_{\mathrm{f},j-1}}\right] \tag{8}$$

The relaxation function is then calculated from

$$\delta(t) = \Delta\alpha \cdot [T_{\mathrm{f},n}(t) - T] \tag{9}$$

To ensure linearity, the intervals Δt_j must be small enough that T_f decays by less than about 0.1 K. Dividing the annealing time into 100 increments per decade of time was found to be satisfactory for the purpose of numerical simulations used here.

The TNM equation has been extensively tested in numerous studies (many of them are quoted in [6,10]) and successfully applied to predict the relaxation response to arbitrary and more complex thermal histories. The parameters β, x, $\ln A$ and Δh^* can be evaluated from experimental data by numerical curve fitting technique [6,9] or by means of the peak-shift method [12,13]. These methods have been successfully applied to many polymeric and inorganic glass forming systems [6,7].

2.3. Stabilization period of the volume relaxation

Fig. 1(b) shows the typical relaxation curve plotted on logarithmic time scale. Stabilization period of the relaxation process is defined by $\log(t_\mathrm{m}/t_0)$ and it can also be expressed through the inflectional slope of the relaxation curve:

$$-\left(\frac{\mathrm{d}\delta}{\mathrm{dlog}t}\right)_{\mathrm{inf}} = \frac{\delta_\mathrm{i}}{\log(t_\mathrm{m}/T_0)} \tag{10}$$

It can be shown by numerical simulation of $\delta(\log t)$ curves that near the inflection point the reduced time can be approximated as $\xi \approx (t/\tau)_{\mathrm{inf}}$. Differentiation of Eq. (6) with respect to $\ln t$ then yields

$$\left(\frac{\mathrm{d}\delta}{\mathrm{dln}t}\right)_{\mathrm{inf}} = -\beta \cdot \left[1 + \frac{(1-x)\Delta h^*}{\delta_i \cdot RT^2_{\mathrm{f,inf}}}\left(\frac{\mathrm{d}\delta}{\mathrm{dln}t}\right)_{\mathrm{inf}} \cdot \Delta T\right] \cdot \xi^{\beta}\delta_{\mathrm{inf}} \tag{11}$$

where the subscript *inf* refers to the inflection point. By numerical simulations it was verified that at the inflection point $(\xi^{\beta}\delta_{\mathrm{inf}}) \cong \delta_\mathrm{i}/e$. Then from Eq. (11) one can obtain an expression for $-\delta_\mathrm{i}/(\mathrm{d}\delta/\mathrm{dln}t)_{\mathrm{inf}}$ at the inflection point:

$$-\frac{\delta_\mathrm{i}}{(\mathrm{d}\delta/\mathrm{dln}t)_{\mathrm{inf}}} = \frac{e}{\beta} + (1-x)\theta_{\mathrm{inf}} \cdot \Delta T \tag{12}$$

where

$$\theta_{\mathrm{inf}} = \frac{\Delta h^*}{RT^2_{\mathrm{f,inf}}} \tag{13}$$

For a moderate temperature jumps near T_g (where T_f do not change rapidly with time) it is possible to assume that this quantity is approximately equal to the KAHR parameter $\theta = \Delta h^*/RT_\mathrm{g}^2$ [5]. The value of θ is a characteristic constant for a particular non-crystalline material [6], generally being of order of unity for polymers and 0.1–0.3 for inorganic glasses.

Combining Eq. (10) and Eq. (12) then follows for the stabilization period of the relaxation process:

$$\log\left(\frac{t_\mathrm{m}}{t_0}\right) = \frac{1.18}{\beta} + \frac{(1-x)\theta}{2.303} \cdot \Delta T \tag{14}$$

The Eq. (14) predicts that for a small temperature jumps (i.e. $\Delta T \rightarrow 0$) non-linearity contribution is small (as mentioned in Section 1) and the second term in Eq. (14) can be neglected. In this case, the stabilization period will be inversely proportional to the non-exponentiality parameter, $\log(t_\mathrm{m}/t_0) \cong 1.18/\beta$. At higher temperature departures from T_0, however, the stabilization period linearly increases with temperature with slope depending on both x and θ parameters. This behavior has an important consequences for prediction of relaxation response in various non-crystalline materials and it is further discussed in Section 3.

2.4. Volume relaxation rate

The volume relaxation rate β_V can be defined as the inflectional slope of the relaxation curve:

$$\beta_V = -\frac{1}{V_0}\cdot\left(\frac{\mathrm{d}V}{\mathrm{dlog}t}\right)_{\mathrm{inf}} \cong -\left(\frac{\mathrm{d}\delta}{\mathrm{dlog}t}\right)_{\mathrm{inf}} \qquad (15)$$

This parameter characterizing the relaxation process was introduced by Kovacs [2,3] and it is often used to compare the relaxation kinetics in various non-crystalline materials [2,7,14,15,20].

According to Eq. (15) and Eq. (10) the volume relaxation rate β_V is proportional to the initial departure from equilibrium and inversely proportional to the stabilization period. Combining Eqs. (2), (10), (14) and (15) the temperature dependence of the volume relaxation rate for TNM model can be expressed as

$$\beta_V(\Delta T) = \Delta\alpha\cdot\left[\frac{1.18}{\beta\cdot\Delta T}+\frac{(1-x)\theta}{2.303}\right]^{-1} \qquad (16)$$

This equation predicts increasing volume relaxation rate with the magnitude of the temperature jump ΔT. The absolute value of β_V is then controlled by $\Delta\alpha$ and parameters β and $(1-x)\theta$. For a constant $\Delta\alpha$, the value of volume relaxation rate decreases with increasing $(1-x)\theta$ and this effect more gradual for lower values of the non-exponentiality parameter β. Nevertheless, the influence of this parameter becomes less important for $(1-x)\theta>0.7$.

The magnitude of volume relaxation rate for constant ΔT can be used to compare the relaxation kinetics in various non-crystalline materials. However, the problem of such comparison is that according to Eq. (16) the β_V depends not only on parameters characterizing the relaxation kinetics (β, x and θ) but also on the $\Delta\alpha$. This should be taken into account when the volume relaxation rate is correlated with TNM parameters for different materials.

3. Results and discussion

The practical application of the analysis described in Section 2 is discussed first with respect to numerically calculated $\delta(\log t)$ curves and then the discussion is extended to the analysis of previously reported isothermal volume relaxation data of polyvinylacetate (PVA) [3] and arsenic sulfide glass (As_2S_3) [19].

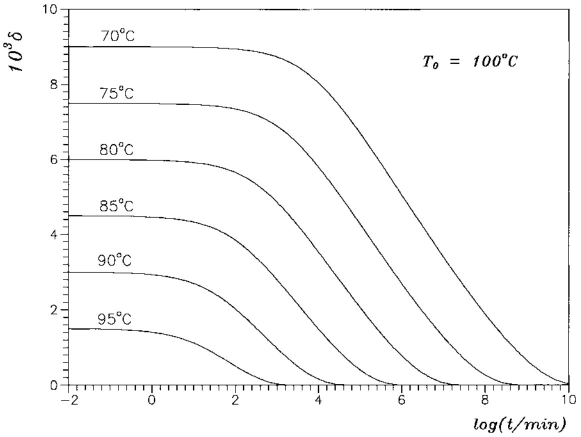

Fig. 2. Isothermal relaxation curves of a stabilized non-crystalline material subjected to a temperature jump from T_0=100°C to T (marked by numbers). These curves were calculated using Eqs. (7)–(9) for $\Delta\alpha=3\cdot10^{-4}\ \mathrm{K}^{-1}$ and TNM parameters: $\Delta h^*/R$= 80 kK, ln(A/min)=−212, x=0.5 and β=0.7. The initial time corresponds to 0.0001 min.

Fig. 2 shows the isothermal relaxation curves at temperatures 70–95°C calculated using Eqs. (7)–(9) for initial temperature T_0=100°C, $\Delta\alpha=3\times10^{-4}\ \mathrm{K}^{-1}$ and the following TNM parameters:

$$\begin{aligned}\Delta h^*/R &= 80\ \mathrm{kK}\\ \ln(A/\mathrm{min}) &= -212\\ x &= 0.5\\ \beta &= 0.7\end{aligned}$$

Initial time for numerical simulation was fixed as $t_i=10^{-4}$ min. These relaxation curves were analyzed using inflectional tangent in a way suggested in Fig. 1(b), which is called here inflectional analysis. The results are shown in Figs. 3 and 4. It is evident that the stabilization period increases linearly with temperature departure from T_0 as anticipated by Eq. (14). The slope of this dependence can be expressed as

$$+\frac{\mathrm{dlog}(t_m/t_0)}{\mathrm{d}\Delta T}=\frac{(1-x)\theta}{2.303} \qquad (17)$$

The time required to reach volume equilibrium as characterized by $\log(t_m)$ increases also linearly with ΔT. Because close proximity to the equilibrium state the non-linearity effects are very small and then the

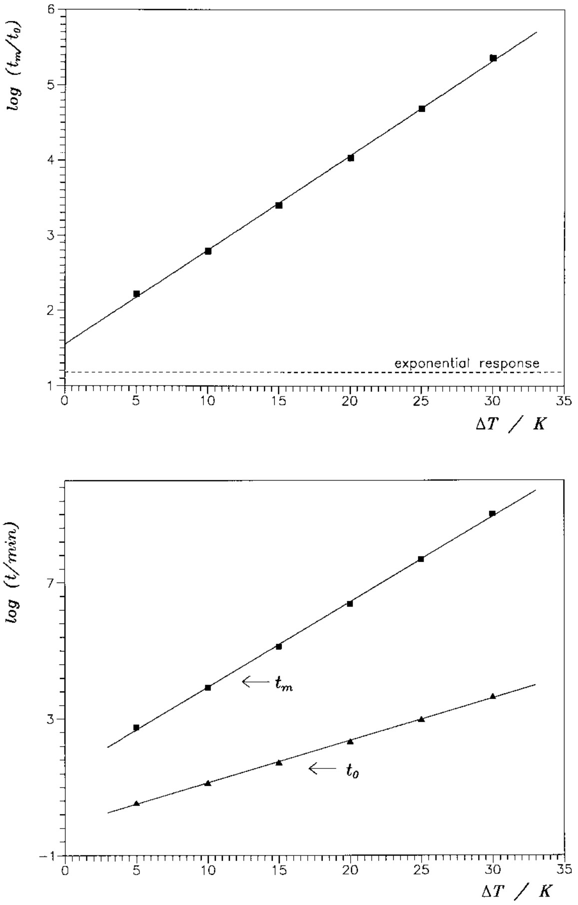

Fig. 3. The temperature dependencies of (a) $\log(t_m/t_0)$ and (b) $\log(t_0)$, $\log(t_m)$ obtained by inflectional analysis of the relaxation curves shown in Fig. 2 (points). The broken line corresponds to the exponential response (i.e. $\log(t_m/t_0)=1.18$). Full lines are linear fits to data points.

slope of this dependence will be

$$+\frac{\mathrm{d}\log(t_m)}{\mathrm{d}\Delta T}\cong\frac{\theta}{2.303} \tag{18}$$

On the other hand, the non-linearity effect are very important for the time $\log(t_0)$ which characterizes the end of curved initial part of relaxation curve where the volume starts to decrease practically linearly with logarithmic time. It can be shown that $\log(t_0)$ increases linearly with temperature departure from T_0 and the slope of this dependence can be expressed as:

$$+\frac{\mathrm{d}\log(t_0)}{\mathrm{d}\Delta T}\cong\frac{x\cdot\theta}{2.303} \tag{19}$$

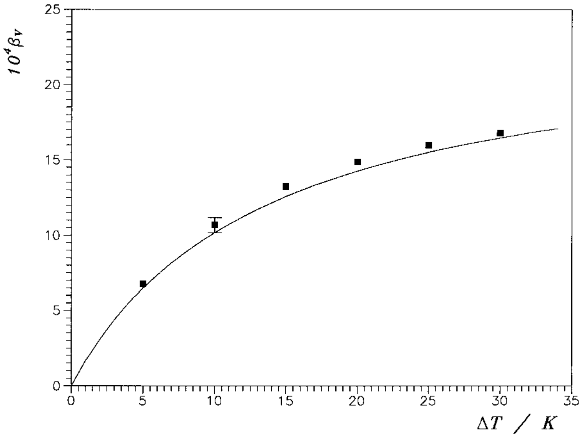

Fig. 4. The temperature dependence of the volume relaxation rate obtained by inflectional analysis of the relaxation curves shown in Fig. 2 (points). Full line was calculated using Eq. (16).

Therefore, comparing the slopes of temperature dependencies of $\log(t_m/t_0)$ and $\log(t_m)$ or $\log(t_0)$ vs. ΔT the parameters θ and x can easily be obtained. The values calculated from the slopes of these plots shown in Fig. 3 are $x=0.50$ and $\theta=0.57\ \mathrm{K}^{-1}$. Eq. (14) also predicts that the intercept of the $\log(t_m/t_0)$ vs. ΔT dependence is $1.18/\beta$ suggesting the possibility of evaluation of non-exponentiality parameter β. The value found from data shown in Fig. 3 is $\beta=0.75$. This value of parameter β is slightly overestimated. On the other hand, the inflectional analysis gives the value of parameter x which agrees well with the non-linearity parameter used for numerical simulation of $\delta(\log t)$ curves.

It should be emphasized, however, that the initial time used for these computer simulated experiments is relatively short ($t_i=10^{-4}$ min). In real temperature jump experiments the first reliable data are obtained after considerably longer times needed to reach thermal equilibrium. For classical mercury-filed glass dilatometry this initial time depends on particular construction details, temperature and magnitude of temperature jump ΔT. It ranges typically from 0.3 to 3 min [3,14–18]. For length dilatometry t_i is generally longer, ranging from 5 min to about 50 min [14,19,20]. Therefore, for a reliable inflectional analysis it is extremely important to choose properly the initial temperature T_0. If T_0 is too high then the relaxation response immediately after the quench will

Table 1
The results of inflectional analysis of calculated relaxation curves $\delta(\log t)$ shown in Fig. 3

t_i (min)	x	β
0.0001	0.50	0.75
0.1	0.49	0.78
0.5	0.48	0.81
1	0.47	0.84
5	0.44	1.00
10	0.41	1.17

be very fast and important part of relaxation occurs before t_i is reached. In this case the first part of relaxation curve will be truncated and inflectional analysis of such data cannot give reliable values of parameters x and β. This is illustrated in Table 1 showing the parameters obtained by the inflectional analysis of calculated relaxation curves (see Fig. 2) for different t_i. It can be shown that a reliable value of parameter x (i.e. within error lower than ± 0.05) can be obtained if $t_i < t_0(T_0)$. The parameter β is even more sensitive in this respect and a reliable value with comparable precision is obtained only for about one order shorter values of the initial time. i.e. $t_i < t_0(T_0)/10$. The value of $t_0(T_0)$ can be estimated from the equation:

$$t_0(T_0) = t_m(T_0) \cdot \exp(-e/\beta) \qquad (20)$$

This equation follows from Eq. (14) for $\Delta T \to 0$. The time required to reach volume equilibrium at initial temperature $t_m(T_0)$ can easily be determined by extrapolation of experimental $\log(t_m)$ vs. ΔT dependence to zero. The exponential term $\exp(-e/\beta)$ ranges from 0.005 to 0.03 for the most typical values of parameter β. For our numerically simulated data it was found that $t_m(T_0)=26.7$ min. Eq. (20) then gives value $t_0(T_0)=0.5$ min. Therefore, reliable values of parameter x can be expected for $t_i<0.5$ min. Similarly, reliable value of parameter β is expected for $t_i<0.05$ min, which is also observed (see Table 1).

Thus, the stabilization period is quite sensitive with respect to the initial time t_i inevitably associated with any real temperature jump experiment. On the other hand, the volume relaxation rate β_V, as defined by Eq. (15) is practically not influenced by the truncation of the first part of relaxation curve. Fig. 4 shows β_V values (points) obtained by inflectional analysis of numerically simulated $\delta(\log t)$ curves (see Fig. 2). Full line was calculated using Eq. (16) for TNM parameters used to simulate $\delta(\log t)$ curves. It is seen that there are some discrepancies between the volume relaxation rate obtained by inflectional analysis and the prediction of Eq. (16). Nevertheless, these discrepancies do not exceed 5%.

Figs. 5–7 shows the results of inflectional analysis (plotted as points, ■, □) for isothermal volume

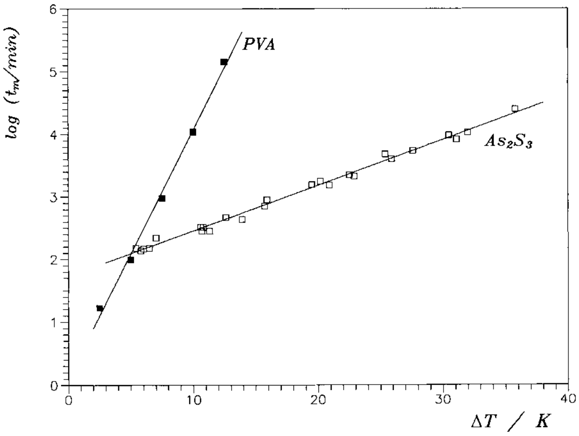

Fig. 5. The $\log(t_m)$ as a function of temperature departure from T_0 for PVA (■) T_0=40°C [3] and As_2S_3 glass (□) T_0=188°C [19]. Full lines are linear fits to experimental data.

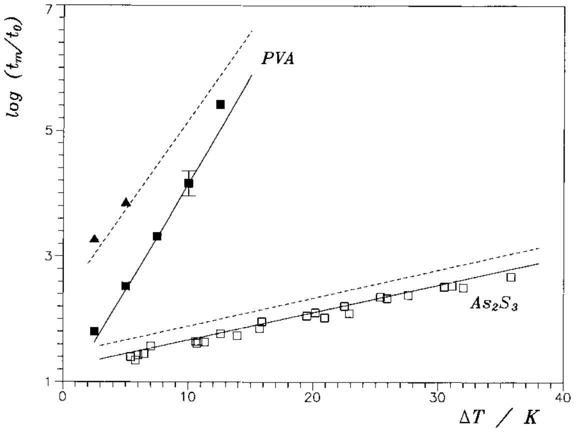

Fig. 6. Stabilization period $\log(t_m/t_0)$ as a function of temperature departure $\Delta T = T_0 - T$ for PVA (■) T_0=40°C, (▲) T=30°C [3] and As_2S_3 glass (□) T_0=188°C [19]. Full lines were obtained by inflectional analysis of relaxation curves calculated for TNM parameters (Table 2) assuming t_i=0.6 and 5 min, respectively. Broken lines were calculated using Eq. (14).

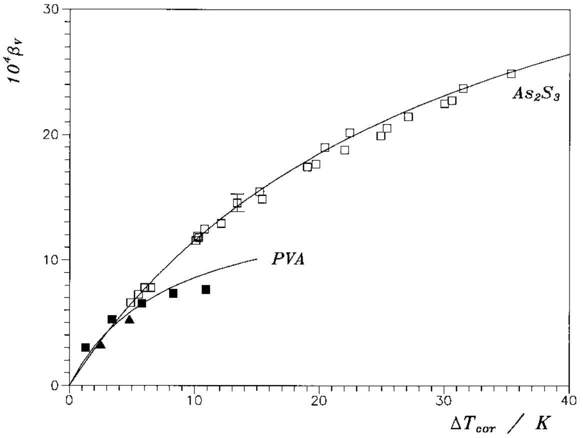

Fig. 7. The volume relaxation rate as a function of corrected temperature departure ΔT for PVA (■) T_0=40°C, (▲) T=30°C [3] and As_2S_3 glass (□) T_0=188°C [19]. Full lines were calculated using Eq. (16) for TNM parameters shown in Table 2.

relaxation of PVA [3], and As_2S_3 glass [19]. These data were obtained after temperature jump from T_0=40°C (PVA) and T_0=188°C (As_2S_3), respectively. The slope of the log(t_m) vs. ΔT dependence for PVA shown in Fig. 5 gives value of parameter θ=0.86 K^{-1}. This value is higher than value reported by Sasabe and Moynihan [21] (θ=0.74 K^{-1}) but relatively close to value reported by Hodge [22] (θ=0.92 K^{-1}) for enthalpy relaxation of PVA. The TNM parameters obtained by curve fitting technique of enthalpy relaxation data of PVA [22] are shown in Table 2. The time $t_m(T_0)$ determined by extrapolation of experimental log(t_m) vs. ΔT dependence was found to be about 1 min. According to Eq. (20) and assuming that β=0.51 this corresponds to $t_0(T_0)$=0.005 min which is far below the initial time t_i reported for these experiments ($t_i \cong 0.6$ min) [3]. It means that relatively large part of relaxation curve was truncated which also explains that δ_i values experimentally observed by Kovacs [3] were considerably lower than expected from Eq. (2). To simulate this situation the δ(log t) curves were calculated for TNM parameters for enthalpy data (see Table 2) and then the first part of these curves corresponding to t_i=0.6 min was truncated. Obtained data were treated by inflectional analysis and the result is shown in Fig. 6 by full line. It is evident that calculated curve follow reasonably well experimental data. Nevertheless, corresponding parameter x=0.13 is strongly underestimated and parameter β=1.55 is evidently overestimated in comparison with TNM parameters used for calculation. Obviously, this is a consequence of truncating important part of δ(log t) curve. The broken line in Fig. 6 corresponds to the log(t_m/t_0) vs. ΔT plot calculated by means of Eq. (14) using TNM parameters for PVA. These values of the stabilization period can be expected if T_0 is sufficiently low to keep the condition $t_i < t_m(T_0)\exp(e/\beta)$ fulfilled. It can be find from Eq. (20) and log(t_m) vs. T plot that this condition is valid for $T_0 \leq 35$°C. Such experiments for PVA were performed by Kovacs [3] for T_0=35°C, T_0=32.5°C and T=30°C. Corresponding log(t_m/t_0) vs. ΔT data are shown in Fig. 6. (points ▲). In this case the experimental data agree well with theoretical prediction from Eq. (14).

The slope of the log(t_m) vs. ΔT dependence for As_2S_3 is shown in Fig. 5 gives value of parameter θ=0.16 K^{-1}. This value well corresponds to the value found by the peak shift method (θ=0.13 K^{-1}) and viscosity measurements (θ=0.15 K^{-1}) [19]. The TNM parameters obtained by curve fitting of volume relaxation data As_2S_3 glass [19] are shown in Table 2. The time $t_m(T_0)$ determined by extrapolation of experimental log(t_m) vs. ΔT dependence was found to be about 58.2 min. According to Eq. (20) and assuming that β=0.82 this corresponds to $t_0(T_0)$=2.1 min which is roughly comparable with the initial time t_i used for these experiments ($t_i \cong 5$ min) [19]. Some part of the

Table 2
The volume thermal expansion coefficients and TNM parameters for structural relaxation of polyvinylacetate (PVA) and arsenic sulfide glass (As_2S_3)

Material	$10^4\Delta\alpha$ (K^{-1})	($\Delta h^*/R$) (kK)	x	β	ln(A/min)	θ (K^{-1})	Ref.
PVA	4.50	88.0	0.27	0.51	−281.6	0.92	[22]
As_2S_3	2.22 [a]	32.4	0.31	0.82	−66.2	0.15	[19]

[a] This value was calculated assuming that $\Delta\alpha=3\Delta\alpha_L$, where α_L is linear thermal expansion coefficient obtained by length dilatometry [19].

relaxation curve will be truncated also in this case but the experimental error is considerably less than for PVA data. To simulate this situation the $\delta(\log t)$ curves were calculated for TNM parameters [19] shown in Table 2 and then the first part of these curves corresponding to $t_i=5$ min was truncated. Obtained data were treated by inflectional analysis and the result is shown in Fig. 6 by full line. The non-linearity parameter calculated by this method, $x=0.33$ is very close to the value found by curve fitting technique (see Table 2). On the other hand, calculated non-exponentiality parameter $\beta=0.96$ is overestimated because in this case $t_i \gg t_0(T_0)/10$. The broken line in Fig. 6 corresponds to the $\log(t_m/t_0)$ vs. ΔT plot calculated by means of Eq. (14) using TNM parameters for As_2S_3 glass. This line is vertically shifted with respect to the $\log(t_m/t_0)$ vs. ΔT plot obtained for $t_i=5$ min but its slope is practically unchanged.

From the previous discussion it is evident that the stabilization period $\log(t_m/t_0)$ can be used as a parameter characterizing the kinetics of the isothermal volume relaxation process. According to Eq. (14), the value of this parameter is determined by non-linearity parameter x, non-exponentiality parameter β and parameter θ. It was shown than for PVA the stabilization period of volume relaxation can be predicted using parameters obtained from enthalpy relaxation data if $T_0 \leq 35°C$. This conclusion should not be generalized, however, as the volume and enthalpy relaxation need not necessarily reflect the same structural changes which may be manifested by different values of x and β [9,23]. Such direct comparison of volume and enthalpy relaxation kinetics is also complicated by some experimental problems. If the initial time for temperature jump experiments becomes comparable with $t_m(T_0)\exp(e/\beta)$ then the measured stabilization period may be underestimated and therefore parameters x and β obtained by inflectional analysis based on Eq. (14) would be different from real ones. Such possible differences should also be taken into account when the stabilization period for isothermal volume and enthalpy relaxation are compared. On the other hand, results of many workers indicate that the effective activation energy is closely related to the viscosity [6] and therefore one can expect that the parameter θ will be very similar for enthalpy and volume relaxation at least at moderate temperature departures from T_g [24]. As noted in Section 2, the values of this parameter are close to 1 for polymers and about 0.1–0.3 for inorganic materials. If the value of parameter x for two non-crystalline materials are comparable (e.g. for PVA and As_2S_3) then it can be expected that the temperature dependence of the stabilization period will be mostly determined by the parameter θ as clearly seen in Fig. 6.

Another parameter which can be used for the comparison of relaxation kinetics in various non-crystalline materials is the volume relaxation rate β_V defined by Eq. (15). As anticipated in Section 2.4 this parameter is expected to be less sensitive with respect to the initial time used for temperature jump experiment. Fig. 7 shows the volume relaxation rates as a function of ΔT_{cor} obtained from previously reported $\delta(\log t)$ data for PVA [3] and As_2S_3 glass [19]. The ΔT_{cor} is defined as the temperature departure from the fictive temperature after the initial time t_i has elapsed. This correction was calculated using Eq. (7). It is seen that $\beta_V(\Delta T)$ data for PVA are not so sensitive with respect to T_0 as it was observed for the stabilization period. Full lines were calculated using Eq. (16) for the parameters shown in Table 2. Experimental and calculated $\beta_V(\Delta T)$ data agree well for As_2S_3 glass ($\Delta T<40°C$) within the limits of experimental errors. On the other hand, experimental β_V data for PVA are lower than predicted by Eq. (16) for $\Delta T>10°C$. It should be pointed out, however, that volumetric equilibrium for PVA is extremely difficult to reach within reasonable time scale and experimentally determined volume relaxation rate do not correspond necessarily to true inflectional slope and the β_V values can easily be underestimated. The volume relaxation rate is comparable for As_2S_3 glass and PVA for low temperature departures ($\Delta T<5°C$). In contrast, the β_V becomes considerably higher for As_2S_3 glass than for PVA for higher temperature departures ($\Delta T>10°C$) as a consequence of higher value of the parameter θ for PVA in comparison with As_2S_3 glass. Nevertheless, this difference is smaller than in the case of the stabilization period since the $\Delta\alpha$ for As_2S_3 glass is about two times lower than for PVA. In order to eliminate this implicit dependence of $\Delta\alpha$, it seems to be convenient to normalize the volume relaxation rate with respect to the magnitude of $\Delta\alpha$. The concept of this normalized relaxation rate is discussed elsewhere [25].

4. Conclusions

The rate limiting factors are analyzed for the isothermal volume relaxation in non-crystalline materials subjected to a temperature jump $\Delta T=T_0-T$. The volume relaxation rate per decade of time, i.e ($d\delta/d\log t$) is inversely proportional to the stabilization period defined as $\log(t_m/t_0)$. It was found that the dependence of $\log(t_m/t_0)$ vs. ΔT can be predicted using a simple linear Eq. (14), relating parameters of TNM model (Δh^*, x and β). This equation, however, can be applied only if the initial time for volume relaxation experiment is lower than $t_m(T_0)\exp(e/\beta)$. It is demonstrated that for non-crystalline materials with similar non-linearity (e.g. for PVA and As_2S_3) the temperature dependence of stabilization period is controlled by the parameter $\theta = \Delta h^*/RT_g^2$. Therefore, it can be expected that organic non-crystalline materials exhibit more important changes of stabilization period with temperature than inorganic glasses, provided that the value of parameter x in these materials is comparable.

The volume relaxation rate β_V defined by Eq. (15) is analyzed for the TNM model. It is shown that the relaxation rate increases with the magnitude of temperature jump and its value is controlled by $\Delta\alpha$ and parameters β and $(1-x)\theta$. The influence of the non-exponentiality parameter is less important for $(1-x)\theta>0.7$. For a constant initial departure $\Delta\alpha\Delta T$, the volume relaxation rate decreases with increasing $(1-x)\theta$.

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