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Dilatometric study of structural relaxation in arsenic sulfide glass

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Abstract

Structural relaxation and viscosity of As_2S_3 glass were studied by length dilatometry. The Tool–Narayanaswamy–Moynihan model was successfully applied for the quantitative description of isothermal and isochronal experiments performed within 40°C below T_g. The activation energy of relaxation process is identical within the experimental errors with that of viscous flow which was found to be 267 kJ/mol. The non-linearity and non-exponentiality parameters were evaluated as x=0.31 and β=0.82, respectively. © 1998 Elsevier Science B.V.

Keywords: Dilatometry; Glass; Structural relaxation; Viscosity

1. Introduction

The non-equilibrium state of a glass, characterized by excess thermodynamic quantities (such as volume, enthalpy, etc.) is well known for more than 60 years [1]. Such materials appear to be unstable and there always will be a driving force which attempts to reduce these excess quantities toward equilibrium. It is generally assumed that such macroscopic changes are linked to structural state of a glass and they are often called 'structural relaxation' process [2] which reflects the time required for the 'glassy' structure to rearrange into its new equilibrium configuration. Structural relaxation is usually characterized by volumetric and enthalpic changes monitored by dilatometric and calorimetric measurements.

Tool [3–5] was one of the pioneers in the field of dilatometric measurements of structural relaxation in inorganic glasses performed by a high-precision length dilatometer. He proposed a phenomenology of structural relaxation based on assumption that the relaxation time τ depends not only on the temperature but also on instantaneous structure of glass characterized by means of fictive temperature. Although this model was found to be quite effective in explaining observed non-linearity of structure relaxation, it failed when it was applied to relaxation behavior of materials with more complicated thermal histories. Naraynaswamy [6] made an important contribution by generalizing Tool's model, assuming that any non-equilibrium state is a mixture of several equilibrium states and that the fictive temperature includes all temperature changes 'remembered' in the structure during previous thermal treatment. This model was later formally modified by Moynihan et al. [7] introducing a partitioning parameter x

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that defines degree of non-linearity and it is referred as the Tool–Narayanaswamy–Moynihan (TNM) model. A similar model was developed independently by Kovacs et al. [8] and it is referred as KAHR model.

The TNM model was successfully used for the description of annealing effects and different thermal histories, including cooling and heating on relaxation behavior in many non-crystalline materials [9]. It is assumed that there is a distribution of relaxation times exhibiting thermorheological simplicity, i.e. the shape of the distribution is invariant with respect to temperature. Most of the TNM model tests have not been done far from the equilibrium. However, Scherer in his remarkable paper [10] successfully explained volume relaxation data of oxide glasses showing that the TNM phenomenology is quite good for describing relaxation kinetics ca. 100°C below T_g.

The main objective of this paper is to illustrate the possibilities of high-precision length dilatometry in the study of structural relaxation of As_2S_3 glass. Structural relaxation data obtained by this technique are described within the TNM theory for temperatures well below the glass transition.

2. Theory and data evaluation

Fig. 1(a) shows the schematic temperature–length plot in the glass-transition region. On cooling from equilibrium, the length of a glassy specimen will depart from the equilibrium line at temperature T_g (which depends on the cooling rate). Isothermal annealing at a temperature T will then cause length contraction from the original specimen length l_0 (immediately after cooling), gradually approaching equilibrium length l_∞ at that temperature.

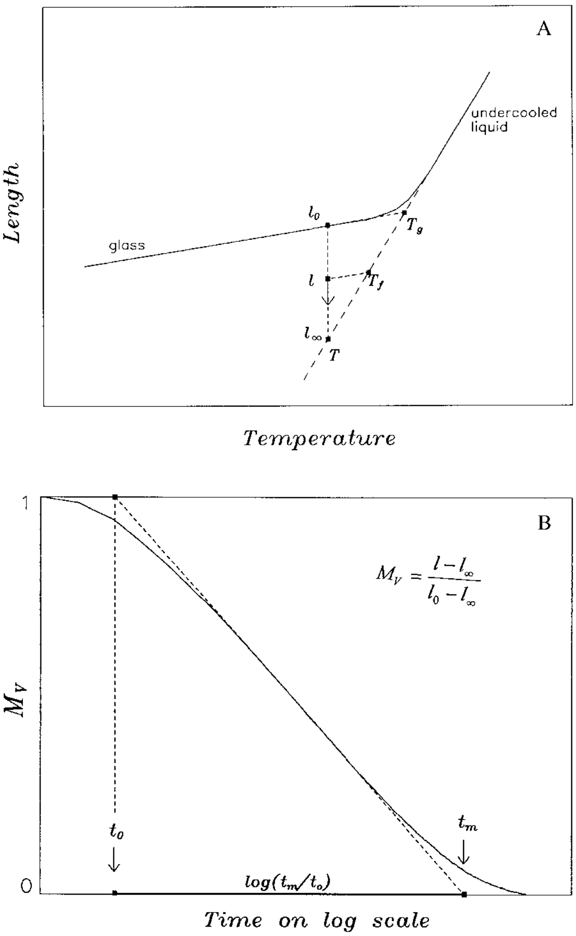

Fig. 1. (a) Schematic illustration of the variation of length in the glass-transition range. Full line shows the cooling curve from a temperature well above T_g. Dotted lines show length and fictive temperature changes of a glass during isothermal annealing at a temperature T. (b) Typical relaxation curve $M_V(t)$ corresponding to isothermal annealing at temperature T. The inflectional tangent (- - -) intersects the ordinates one and zero corresponding to values of times t_0 and t_m, respectively.

Isothermal structural relaxation can be expressed as the relative departure of actual specimen length l from the original specimen length l_0 corresponding to a glass prepared by a constant cooling rate q_l from undercooled liquid:

$$\Delta = \frac{l - l_0}{l_0} \tag{1}$$

For the relative departure from equilibrium it then follows: $\Delta_\infty = (l_\infty - l_0)/l_0$. Consistently with Fig. 1(a) the ratio of $(l_\infty - l_0)$ and $(T - T_g)$ should be equal to $d(l_0 - l_g)/dT = l_0 \Delta\alpha$, where $\Delta\alpha$ is the difference between the thermal expansion coefficient of equilibrium undercooled liquid α_l and asymptotic value of the thermal expansion coefficient of glass α_g. The relative departure in equilibrium then can be expressed as

$$\Delta_\infty = \Delta\alpha(T - T_g) \tag{2}$$

It is often more convenient to describe the isothermal structural relaxation as a function M_V, scaled within the interval $0 \leq M_V \leq 1$ and defined as

$$M_V(t) = \frac{l(t) - l_\infty}{l_0 - l_\infty} = 1 - \frac{\Delta(t)}{\Delta_\infty} \tag{3}$$

Time dependence of the M_V function is usually plotted on logarithmic time scale as shown in Fig. 1(b). Broken line connects values of times t_0 and t_m at which the inflectional tangent intersects ordinates at one and zero, respectively. The structural relaxation of glasses is slower than exponential [2] and the stabilization period as determined by $\log(t_m/t_0)$ is always larger than of a single exponential decay for which $\log(t_m/t_0) \approx 1.18$. This self-delaying process could be explained by implicit dependence of relaxation time upon actual structure of amorphous material (non-linearity) as well as by distribution of relaxation times (non-exponentiality).

The non-linearity arises from the dependence of structural relaxation time τ on the temperature T and the actual structure of a glass which means that the stabilization period of the relaxation process depends strongly on the initial departure from the equilibrium. A generalized expression of this dual dependence of τ is often expressed in the form of the Tool–Narayanaswamy–Moynihan (TNM) equation [2,9]:

$$\tau = A \cdot \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{4}$$

in which the structure is characterized by the fictive temperature T_f defined as the temperature at which the specimen length would be equal to the equilibrium length (see Fig. 1(a)). Eq. (4) introduces three constant parameters: the non-linearity parameter x ($0 < x \leq 1$), the activation energy Δh^* and the pre-exponential factor A. According to the Naraynanaswamy [6] linearity can be restored using the reduced time defined by

$$\xi = \int_0^t \frac{dt}{\tau(T,t)} \tag{5}$$

If a glass is equilibrated at temperature T_0 and then subjected to sudden temperature change to temperature T then the relaxation function M_V is expressed as

$$M_V(\xi) = \frac{T_f(t) - T}{T_0 - T} \tag{6}$$

This equation, however, applies only for step changes in temperature that are so rapid that $T_f(0) = T_0$. If the temperature during cooling of the glass changes gradually then the corresponding thermal history should be taken into account [6,10,11]. In order to simplify the problem it is possible to assume that the sample is cooled in equilibrium to temperature T_g and then instantly cooled to temperature T. Therefore, the fictive temperature at the beginning of isothermal annealing is equal to T_g (see Fig. 1(a)) and during the relaxation process it gradually approaches the annealing temperature according to the following equation where $\Delta T = T_g - T$.

$$T_f = T_g - \Delta T \cdot [1 - M_V(\xi)] \tag{7}$$

The non-exponentiality may be introduced into Eq. (7) either by means of a stretched exponential function [9–11]:

$$M_V(\xi) = \exp(-\xi^\beta) \tag{8}$$

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, for example in the KAHR model [8].

The Eqs. (4)–(8) are sufficient to describe quantitatively the response (volume, enthalpy, etc.) of a glass to isothermal treatment below T_g. The parameters β, x, A and Δh^* can be evaluated from experimental data by numerical curve fitting technique [7,9] or by means of the peak-shift method [12,13]. These methods has been successfully applied to polymeric [14–18] and inorganic [19–23] glass forming systems.

The evaluation of parameters involves numerical evaluation of reduced time integral (Eq. (5)) which is accomplished by dividing total aging time into sufficient number of subintervals Δt_i and calculating corresponding change of T_f at the end of each subinterval [24,10]. The Eq. (7) then can be expressed as

$$T_{f,n} = T_g - \Delta T\left(1 - \exp\left[-\left(\sum_{i=1}^{n}\frac{\Delta t_i}{\tau_i}\right)^\beta\right]\right) \tag{9}$$

where τ_i is given by

$$\tau_i = A\exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_{f,i-1}}\right] \quad (10)$$

The relaxation function is then calculated from

$$M_V(t) = \frac{T_{f,n}(t) - T}{T_0 - T} \quad (11)$$

To ensure linearity, the intervals Δt_i must be small enough so that T_f decays by less than ca. 0.1 K. Dividing the annealing time into 100 increments per decade of time was found to be satisfactory.

A computer program was written to perform these calculations comparing the calculated isothermal relaxation curve to the experimental data, and adjust the parameters to improve fit. As a result of this computer fitting procedure the values of parameters A, x and β were obtained. The parameter Δh^*/R is not considered as adjustable parameter in these numerical calculations and it can easily be determined, e.g. from the slope of a linear dependence of $\log(t_m)$ plotted as a function of reciprocal temperature [25] (see Section 4.5). This parameter is related to the parameter θ of the KAHR model [12]:

$$\theta = \frac{\Delta h^*}{RT_g^2} \quad (12)$$

The values of the parameter θ are similar for a wide variety of materials [9], generally being of the order of unity for polymers and 0.1–0.3 for inorganic glasses.

The determination of parameter θ is based on the method suggested by Hutchinson and Ruddy [12], involving the use of intrinsic cycles (zero annealing time) in which the ratio of cooling rate q_1 and subsequent heating rate q_2 is maintained constant. The temperature dependence of thermal expansion coefficient on heating then exhibit typical relaxation peak temperature T_p which is shifted as a function of heating rate (see Fig. 3). The parameter θ is then evaluated as a slope of the T_p vs. ln q_2 dependence [12]:

$$\theta^{-1} = \left(\frac{\partial T_p}{\partial \ln q_2}\right)_{q_1/q_2=\text{const}} \quad (13)$$

3. Experimental

3.1. Synthesis

The arsenic sulfide glass was prepared in a sealed fused silica ampoule because of the relatively high vapor pressure exhibited by sulfur at higher temperatures as well as to minimize water and oxygen contamination of material prepared. Fused silica ampoules used for synthesis were rinsed prior to batching in redistilled water and then dried at 100°C. Arsenic (5 N purity) and sulfur (Mark DAB-6, purified in the way described in Ref. [26]) were consecutively weighed accurately to ±0.02% into the ampoule, followed by degassing under vacuum before final sealing of the ampoule ($p\approx 10$ mPa).

The batched ampoule was loaded into a furnace which was rocked during melting to improve melt homogeneity. The temperature was then raised to 950°C at which it was maintained for a period of 12 h. After the synthesis the ampoule was air quenched and then annealed for 1 h at 188°C followed by a slow cooling within the annealing furnace. The amorphous nature and composition of prepared ingot were checked by X-ray diffraction and energy dispersive microanalysis. The rectangular specimens were cut off from the ingot for both thermal expansion and structural relaxation experiments. Thin plates (ca. 1 mm thick) were used for the viscosity measurements.

3.2. Dilatometric measurements

For the thermal expansion as well as for the structural relaxation measurements, a thermochemical analyzer TMA CX02R (R.M.I., Czech Republic) was used. The instrument is based on the principle of measurement of changes of the sample length relative to a quartz sample holder with differential capacitance displacement probe detector. The detector is controlled through a unique electronic system which ensures linearity better than 0.1% (full scale), high sensitivity (0.01 μm resolution), low noise (typically 0.02 μm without signal filtering), very good resolution and baseline flatness over broad temperature and time scale range (<0.002 μm/K and 0.008 μm/h, respectively). The temperature of the displacement sensor and some electronic parts is precisely controlled which improves baseline stability and reproducibility. Because of this design and exceptionally low noise level, extremely sensitive measurements can be performed even on a routine basis. As the measuring range of the displacement sensor is >20 mm it is possible to measure height directly and, therefore, it is not necessary to mechanically adjust any part of the analyzer which considerably improves baseline stability and accuracy of measurement. All functions of the TMA instrument, such as tare of the probe, probe loading (0–1 N, step 1 mN) are fully controlled through the computer.

Because of this design and exceptionally low-noise level, very sensitive and reproducible measurements of dimensional changes can be performed. The temperature range of the instrument is from ambient temperature up to 900°C. The absolute error of the temperature measurement, which is determined by K-thermocouple is not greater than ±2°C. The scanning rates can be programmed from 0.1 to 10 K/min. The long term stability of the temperature in the isothermal regime is ±0.2°C and the variation of heating rate does not exceed 1%. In general, the time needed to approach thermal equilibrium in isothermal regime depends on factors such as specimen size, previous scanning rate, temperature, etc. and usually lies between 1–5 min.

All experiments were carried out using rectangular specimens ca. 4×4×10 mm. Surfaces of this specimen were polished to optical quality. To avoid penetration of the probe into the specimen above T_g the measurements were performed with specimen inserted between two parallel quartz plates of 5×5 mm. The dilatometric measurements of the structural relaxation of As_2S_3 glass below T_g were conducted according to the following procedure. First the specimen was heated to a temperature T_0=230°C which is well above T_g. Then the specimen was subjected to cooling with the rate $q_1=-5$ K/min to an annealing temperature $T<T_g$. At this temperature the sample was kept for various annealing time (2, 5, 20 or 50 h) and its length contraction caused by structural relaxation effect was measured as a function of time. The first reliable data on these isothermal measurements are obtained after an initial time t_i=5 min. This time is necessary for thermal equilibration of the sample. After the period of annealing time t_a has elapsed, the specimen was cooled to 80°C at a cooling rate −5 K/min and immediately reheated to a temperature T_0 at a heating rate q_2=3 K/min. This heating scan is used to calculate temperature dependence of thermal expansion coefficient on heating (see Fig. 6). Then the specimen was cooled to another temperature T and the same thermal cycle is repeated again. During these experiments the specimen was loaded by force 10 mN. It was verified that the force up to 100 mN does not affect the length contraction. It has been also confirmed that the magnitude of the relative length changes agrees well for all three dimensions of the rectangular specimen and that the contraction caused by structural relaxation is isotropic. The thermal expansion changes, due to temperature equilibration effects, are negligible ($\Delta\cong 0.04$) with respect to the relaxation response of the material.

3.3. Viscosity measurements

Viscosities of undercooled liquid (10^7–10^{12} Pa s) in the glass-transition range ($T>T_g$) were measured by penetration viscometry using the same equipment as described in Section 3.2. This method is based on a penetration of hemisphere of radius R loaded by a force F into the flat specimen of a glass. The penetration depth l is measured as a function of time t and the viscosity is then determined using following equation [27,28] which holds for $R\gg l$:

$$\eta = \frac{9}{32\sqrt{2R}} \frac{Ft}{l^{3/2}} \tag{14}$$

Therefore, the viscosity may conveniently be determined from the rate of penetration of a hemispherical indenter into the sample, provided that the penetration depth is small as compared with dimensions of the indenter. This method is absolute and thus no calibration is needed. The measurement procedure used by us can be outlined as follows. Flat specimen of a glass ca. 5×5×1 mm (polished to optical quality) is placed in the TMA cell, on top of a quartz plate. A hemispherical quartz indenter (R=1.2 mm) was placed between the probe and the polished specimen surface. The TMA cell was heated at 10 K/min to the required temperature T using loading force of 1 mN. Then 5 min are allowed for thermal equilibration. The force in the range 50–500 mN is applied to the hemispherical indenter and the penetration depth is measured as a function of time (for 1–5 h, depending on the viscosity) once the constant penetration rate is ensured. The force applied to the sample should be chosen to keep the condition $l \ll R$ fulfilled. The viscosity at temperature T is then calculated using Eq. (14). After the measurements the specimen surface was examined by optical microscopy. The verification of this measurement technique has been performed using a National Bureau of Standards glass NBS711 [29] over a range 10^7–10^{12} Pa s.

4. Results

4.1. Viscosity of undercooled liquid

Viscosity measurements of undercooled liquid of As_2S_3 glass (i.e. for $T > T_g$) were performed according to the procedure described in Section 3.3. The temperature dependence of viscosity data of arsenic sulfide undercooled liquid is depicted in Fig. 2. Over the range of 4 orders the plot of log η vs. $1/T$ exhibit a negligible curvature and, therefore, it can be described by a simple Arrhenius behavior. Our data (■) and previously published data of Nemilov et al. [30] (□) are shown in this figure. It is evident that both these data sets exhibit very similar temperature dependencies giving practically identical slopes. From our data a value of the activation energy of viscous flow was found to be $E_\eta = 267 \pm 9$ kJ/mol.

Nevertheless, our data are slightly shifted to higher temperature in comparison with Nemilov's data giving different estimations of viscometric T_g value which conventionally is the temperature corresponding to a viscosity of 10^{12} Pa s. These values, as determined from both data sets, were found to be 185 and 181°C, respectively. This temperature shift is considerably higher than expected uncertainty in the temperature determination (±0.2°C) and therefore it cannot be explained by systematic temperature deviation of our measurements. It should be pointed out, however, that Nemilov's data were obtained by penetration technique using a cylindrical indenter. This method requires a calibration procedure which is not necessary in the case of a hemispherical indenter used in our case. Therefore, it is possible that the slight temperature shift, observed between both data sets, may originate in experimental errors involved in the mentioned calibration routine.

4.2. Evaluation of θ

As has been mentioned in Section 2, the temperature dependencies of thermal expansion coefficient

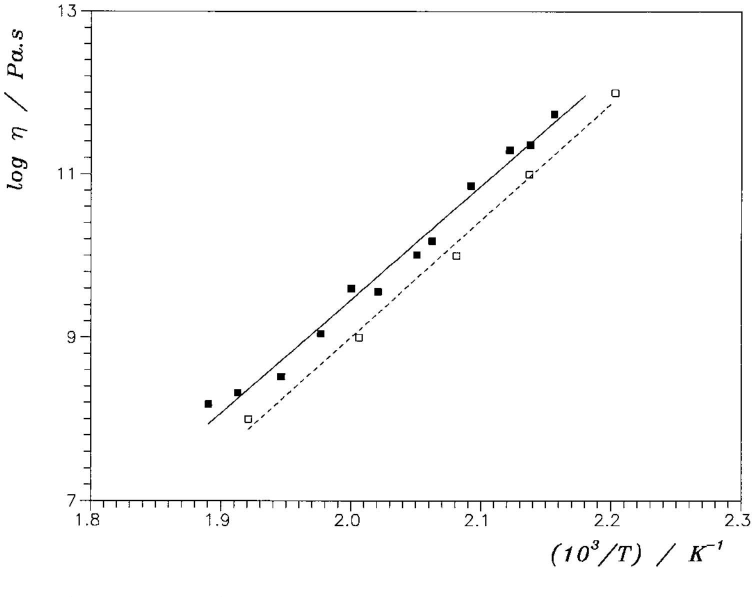

Fig. 2. Temperature dependence of the logarithms of the shear viscosity: our data (■), Nemilov [30] data (□). The straight lines represent the best linear fits to both data sets.

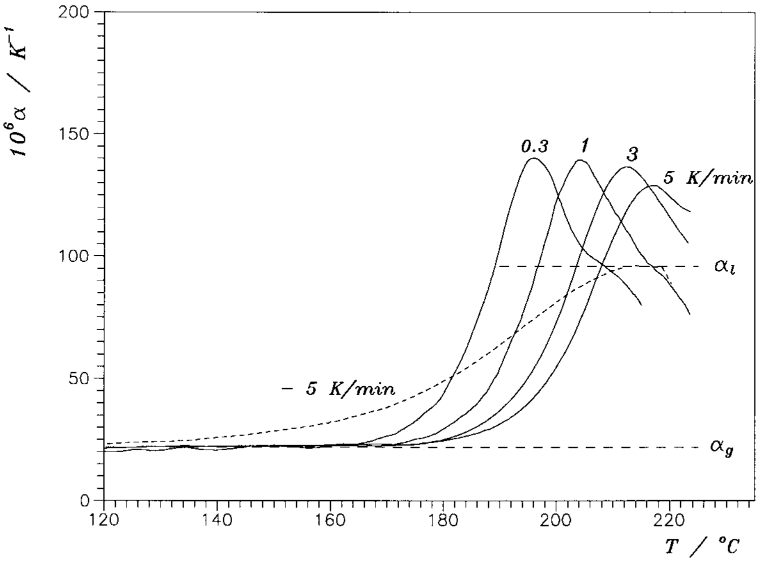

Fig. 3. Temperature dependencies of thermal expansion coefficient of As_2S_3 glass. Heating curves (———) were obtained immediately after previous cooling from temperature T_0=230°C with the same scanning rate (marked by numbers). The cooling curve (· · ·) was obtained by cooling rate $q_1=-5$ K/min. Extrapolated values of thermal expansion of glass (α_g) and undercooled liquid (α_l) are shown by broken lines.

$\alpha(T)$ of a glass display a relaxation peak in T_g region that shows the temperature shift dependent on the thermal history. Current phenomenology predict [12] that, for scans of unannealed glasses for which the ratio of cooling to heating rates q_1/q_2 is kept constant (the so-called intrinsic cycle), the peak of $\alpha(T)$ curves shifts to higher temperatures with increasing heating rate. This behavior is demonstrated in Fig. 3 where full lines correspond to heating curves taken immediately after the cooling curve using exactly same scanning rate, i.e. $q_1/q_2=1$. The peak temperature T_p, on heating, was then determined as a function of heating rate q_2. According to Eq. (13) the parameter θ is then evaluated as an inverse slope of the T_p vs. ln q_2 dependence. From the data in Fig. 3 a value of $\theta=0.14\pm0.01$ K^{-1} is obtained.

This parameter is a very important characteristic of the relaxation process and it can be related to an activation energy of the structural relaxation through Eq. (12). Using this equation, the parameter θ can also be calculated for the activation energy and T_g obtained from viscosity measurements of undercooled liquid (see Section 4.1). The value calculated in this way is $\theta=0.15\pm0.01$ K^{-1} which is very close to the value obtained from intrinsic cycles.

4.3. Evaluation of $\Delta\alpha$ and T_g

For a reliable analysis of structural relaxation data it is essential to correctly determine the thermal expansion of glass α_g and that of undercooled liquid α_l. Their difference $\Delta\alpha=\alpha_l-\alpha_g$ may be assumed constant in the glass-transition range. As the length dilatometry is used here instead, the direct volume measurements, the specimen shape might be slightly deformed above T_g due to viscous flow. Another complication may arise from the structural relaxation taking place during the measurement. To reduce the influence of these effects the thermal expansion of undercooled liquid is measured on cooling using an appropriate cooling rate. If the cooling rate is too small the viscous flow effect during the measurement becomes important and measured thermal expansion coefficient is then usually overestimated. On the other hand, high cooling rates bring problems of temperature equilibration in a specimen. It was found that for our specimen and particular geometry of TMA cell (see Section 3.2) an optimum cooling rate is −5 K/min and measured thermal expansion coefficient of undercooled liquid was found to be $\alpha_l=96\times10^{-6}$ K^{-1} (see Fig. 3).

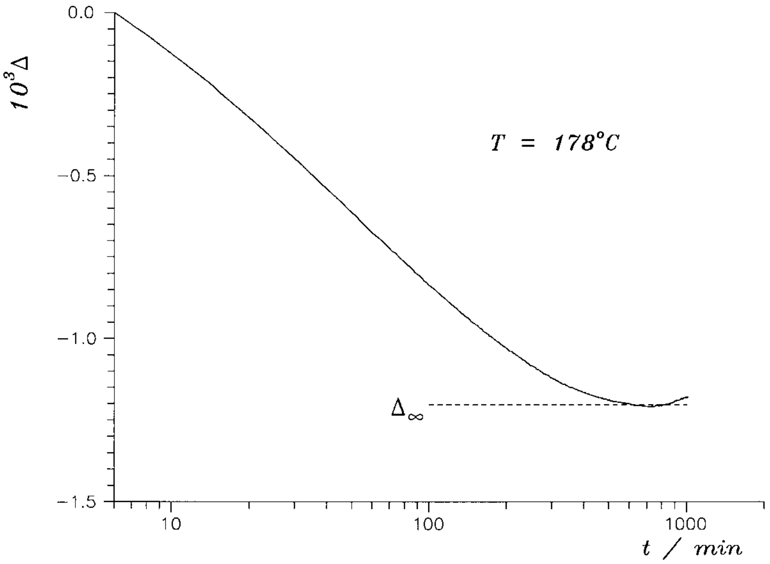

Fig. 4. Time dependence of the relative length contraction of As_2S_3 glass at temperature 178°C (T_0=230°C, q_1=−5 K/min). Extrapolated equilibrium value calculated using Eq. (15) is shown by broken line.

It is seen from Fig. 3 that well below T_g the thermal expansion curves (for heating as well as for cooling) approach the value corresponding to the thermal expansion of As_2S_3 glass, α_g. This value is practically not influenced by structural relaxation effects and it can be determined with considerably higher reproducibility and precision than α_l. For the wide range of cooling and heating rates used here, the thermal expansion coefficient of As_2S_3 glass was found to be constant with value of $\alpha_g=(22.0\pm0.1)\times10^{-6}\,K^{-1}$. Thus, the value of the difference of these thermal expansion coefficients is $\Delta\alpha=74\times10^{-6}\,K^{-1}$.

The glass-transition temperature T_g has been evaluated as the point of intersection of the thermal expansion curves on cooling for the glassy and undercooled liquid states as schematically illustrated in Fig. 1(a). The slopes of the thermal expansion curves, before and after the glass transition, correspond to the values α_g and α_l evaluated above. This procedure gives for As_2S_3 glass subjected to cooling by q_1=−5 K/min the value of T_g=188°C.

4.4. Effects of isochronal annealing below T_g

At sufficiently high temperatures ($T_0>T_g+20$°C) the equilibrium length (l_∞) of the specimen is reached practically instantaneously, whereas in the glass-transition range, the equilibrium is approached more slowly and the time t_m rapidly increases with temperature departure from T_g. Fig. 4 shows isothermal relaxation response of As_2S_3 glass 10°C below T_g measured after cooling from 230°C at −5 K/min. It is seen that the equilibrium is reached after ca. $t_m\approx600$ min. In this way the equilibrium contraction Δ_∞ can be determined at various temperatures not so far below T_g. It was found that the temperature dependence (°C) of equilibrium length contraction of As_2S_3 glass can be expressed as:

$$10^3\Delta_\infty = 0.063\cdot T - 12.41 \qquad (15)$$

Fig. 5 shows the temperature dependence of relative length contraction $\Delta(T)$ for different isochronal time scales (2, 5, 20 and 50 h). It is evident that these isochronal $\Delta(T)$ curves corresponding to various time scales merge at their high temperature limit and they become practically identical with extrapolated equilibrium contraction (———). This extrapolated equilibrium line was calculated using Eq. (15). Small deviations from this line observed at higher temperatures above T_g are probably caused by partial specimen deformations due to non-negligible viscous flow (see Section 4.1). This explanation is also supported

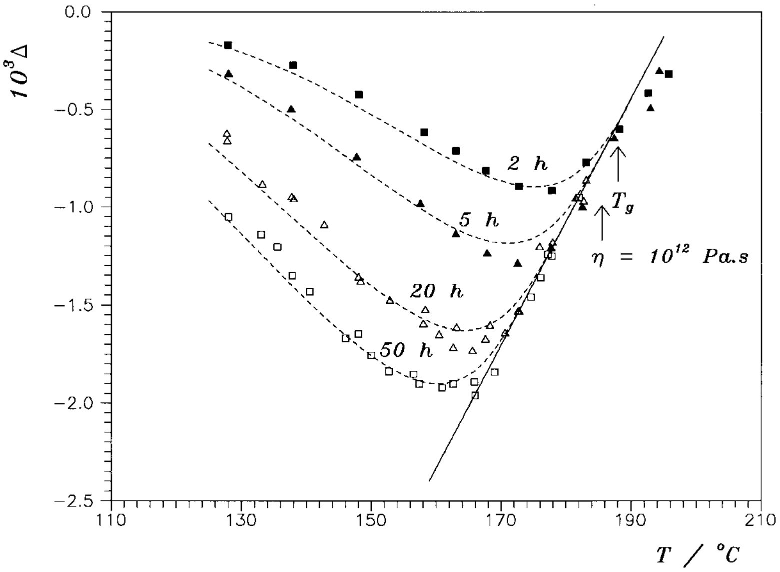

Fig. 5. Isochronal temperature dependence of relative length contraction of As_2S_3 glass (T_0=230°C, q_1=−5 K/min) for different experimental time scales: (■) 2; (▲) 5; (△) 20; (□) 50 h. The broken lines were calculated using Eqs. (9)–(11) and (16) for TNM parameters (Table 1). The extrapolated equilibrium line (———) was calculated using Eq. (15). Temperatures corresponding to the value of viscosity of 10^{12} Pa s and to the glass-transition temperature T_g are marked by arrows.

by a fact that time dependencies of the relative length contraction $\Delta(t)$ near T_g exhibit a slow gradual decrease after reaching limiting value, Δ_∞. Such behavior is seen in Fig. 4 (t >800 min) even 10°C below T_g.

There are systematic deviations of the isochronal $\Delta(T)$ dependencies from the extrapolated equilibrium contraction line (see Fig. 5) as it becomes difficult to reach an equilibrium state within the experimental time scale. Maximum structural relaxation extent for a given time scale is characterized by a minimum of corresponding isochronal $\Delta(T)$ curve. These minima are shifted to lower temperature with increasing isochronal time scale. Such shift suggests the activated process and it can be used to estimate corresponding effective activation energy, which was found to be 289±3 kJ/mol. The broken lines represent theoretical isochronal curves calculated using following equation:

$$\Delta(T) = \Delta_\infty(T)[1 - M_V(T,t)] \qquad (16)$$

where $\Delta_\infty(T)$ was calculated from Eq. (15) and the relaxation function $M_V(T,t)$ from Eqs. (9)–(11) for the best fit TNM parameters (see Table 1). Fig. 5 shows that the data points obtained for different isochronal time scales agree well with the calculated curves, as predicted by TNM model.

Table 1
Parameters for the structural relaxation in As_2S_3 glass

$\Delta h^*/R$ (kK)	32.4±0.5
x	0.31±0.02
β	0.82±0.02
−ln (A/min)	66.2±0.3

If the specimens after described isochronal annealing are immediately reheated by a constant heating rate q_1 above T_g then the thermal expansion coefficient passes through a maximum before equilibrium state is reached again. Such behavior is shown in Fig. 6. These $\alpha(T)$ curves correspond to heating rate q_2=3 K/min performed after isochronal annealing for 50 h at different temperatures followed by cooling to 80°C. Regardless of a different thermal history, all these curves below 140°C merge to one point corresponding to the thermal expansion coefficient of a glass (see Section 4.3). The effect of increasing annealing temperature, while maintaining annealing

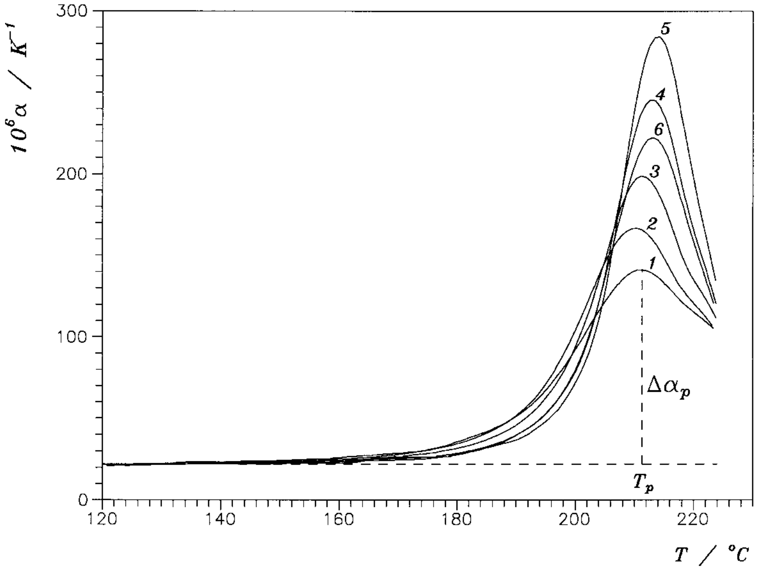

Fig. 6. Temperature dependencies of thermal expansion coefficient of As_2S_3 glass annealed 50 h (T_0=230°C, q_1=−5 K/min, q_2=3 K/min) at various temperatures: (1) 122.7, (2) 133.0, (3) 140.5, (4) 150.0, (5) 160.9, (6) 174.6°C.

time constant, is manifested in the magnitude of thermal expansion peak denoted here as $\Delta\alpha_p$. The $\Delta\alpha_p$ can be considered to be a measure of the structural relaxation taking place during previous isochronal treatment at a given temperature. It is clearly seen that $\Delta\alpha_p$ increases with temperature, then passes through a maximum and finally decreases as shown in Fig. 7 for various isochronal time scales. Broken line in this figure corresponds to the intrinsic cycle when the freshly cooled specimen (q_1=−5 K/min) with erased thermal history was immediately reheated (q_2=3 K/min). This value is ca. 50% higher than the thermal expansion coefficient of undercooled liquid revealing continuation of relaxation process during the described thermal cycle. The appearance of Fig. 7 is very similar to Fig. 5 discussed above. All isochronal curves corresponding to various time scales merge at their high temperature limit practically forming a straight line showing slight curvature in the T_g region. At lower temperatures these $\Delta\alpha_p(T)$ curves exhibit maxima which can be associated with the maximum structural relaxation for particular time scale. From the temperature shift of these maxima it is possible to estimate the effective activation energy which was found to be identical to that obtained from $\Delta(T)$ dependencies discussed above (see Fig. 5).

4.5. Isothermal structural relaxation

Fig. 8 shows typical isothermal structural relaxation data of an arsenic sulfide glass plotted as a function M_V on logarithmic time scale at various temperatures. These $M_V(t)$ dependencies were obtained from experimental data using Eqs. (1),(3) and (15). There are two interesting features, in particular, to observe. First, it is immediately evident that the time required to attain volume equilibrium as characterized by t_m (see also Fig. 1(b)), rapidly increases with decreasing temperature. The variation of $\log(t_m)$ with $1/T$ is shown in Fig. 9. The straight line represents the best linear fit to these data. This observation is in agreement with the fact that for sufficiently long times the fictive temperature approaches the annealing temperature and Eq. (5) then can be expressed as a simple Arrhenius relationship. Therefore, the slope of the straight line in Fig. 9 gives the value of $\Delta h^*/R$=32.4 kK, corresponding to an activation energy of 269±4 kJ/mol. Using Eq. (12) the parameter θ=0.15 K^{-1} can be calculated for this value of activation energy and for T_g=188°C. This value of θ is very close to that evaluated from intrinsic thermal cycles as well as from viscosity data (see Section 4.2).

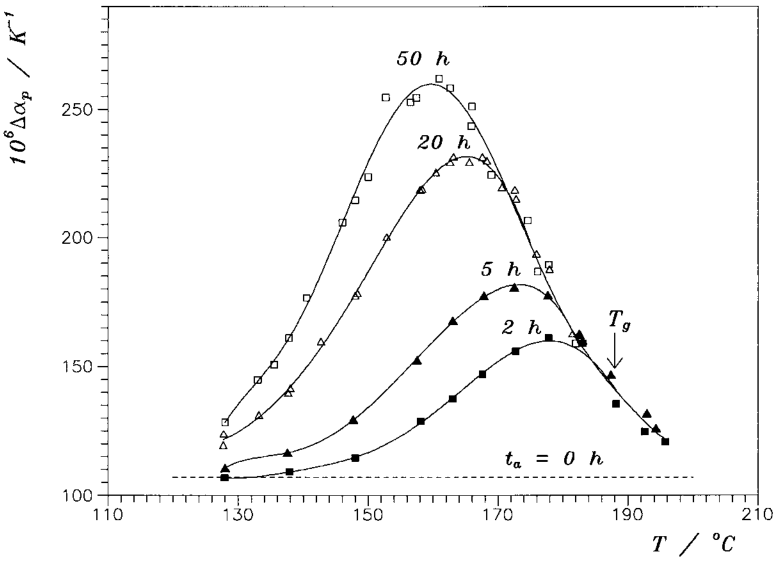

Fig. 7. Isochronal temperature dependence of the magnitude of thermal expansion peak (see Fig. 6) of As_2S_3 glass (T_0=230°C, q_1=−5 K/min, q_2=3 K/min) for different experimental time scales: (■) 2; (▲) 5; (△) 20; (□) 50 h. The full lines are drawn as guides for the eye. The dotted line corresponds to the sample immediately reheated after previous cooling. The glass-transition temperature is marked by an arrow.

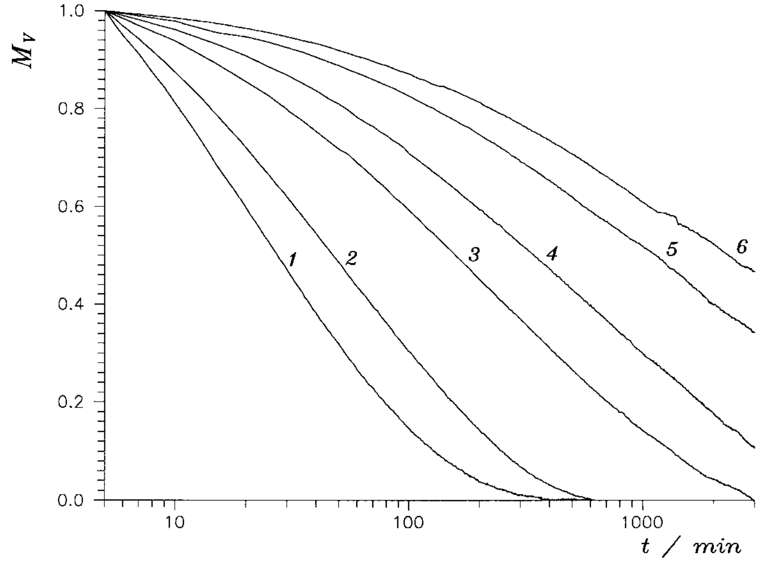

Fig. 8. Isothermal relaxation curves of As_2S_3 glass (T_0=230°C, q_1=−5 K/min): (1) 183.1, (2) 177.9, (3) 169.0, (4) 160.9, (5) 152.7, (6) 148.0°C.

The second important feature of Fig. 8 is that the stabilization period defined as $\log(t_m/t_0)$ is always larger than that of simple exponential response for which it should be close to 1.18 and, moreover, it decreases linearly with temperature. This is illustrated in Fig. 10 where the $\log(t_m/t_0)$ vs. T is shown. By extrapolation of this dependence it is found that the exponential relaxation response occurs at 188.5°C which is very close to the value of T_g for cooling rate −5 K/min (see Section 4.3).

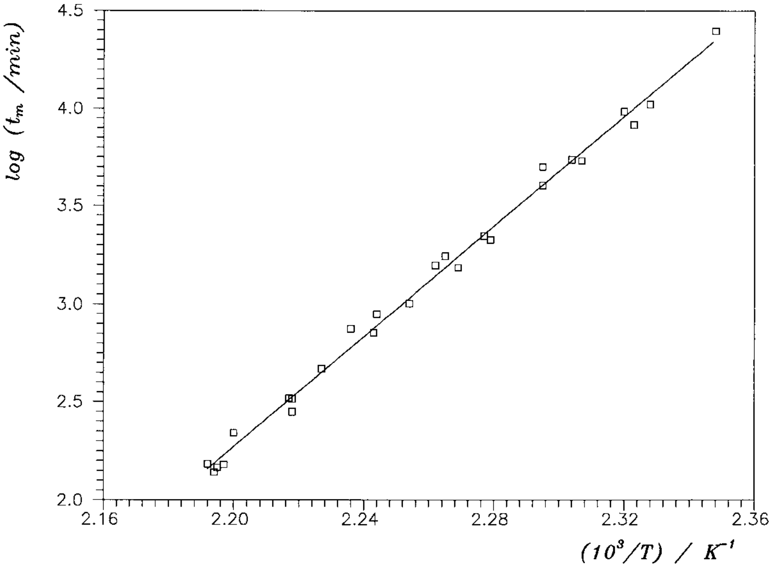

Fig. 9. Logarithm of extrapolated time $t_{\rm m}$ as a function of reciprocal temperature for structural relaxation data of As_2S_3 glass (T_0=230°C, q_1=−5 K/min). Points correspond to experimental data and full line is a linear regression fit to experimental data.

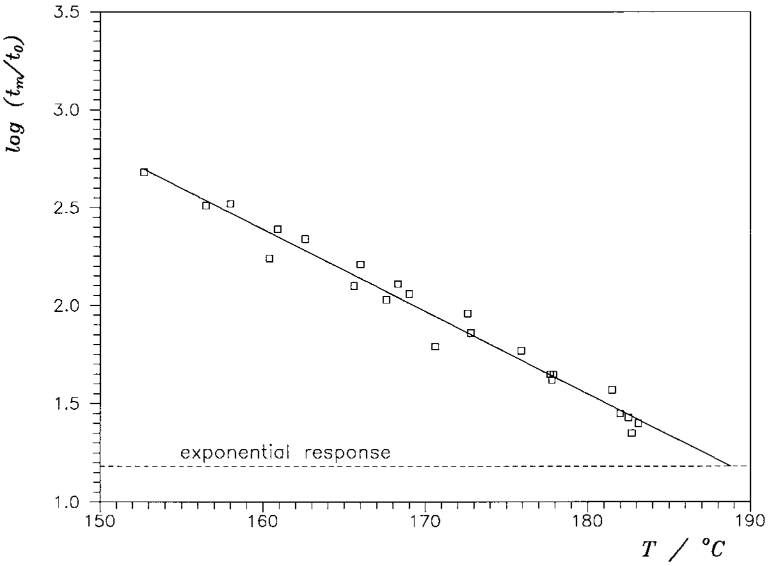

Fig. 10. Temperature dependence of the stabilization period of structural relaxation of As_2S_3 glass (T_0=230°C, q_1=−5 K/min). Points correspond to experimental data and full line is a linear regression fit to experimental data.

The parameters of structural relaxation of arsenic sulfide glass evaluated by the curve fitting method discussed in Section 2 are summarized in Table 1. Fig. 11 shows the comparison of experimental structural relaxation data (□) and $M_{\rm V}(t)$ curves (———) calculated using Eqs. (9)–(11) for various temperatures below $T_{\rm g}$.

For the reasons of clarity, only some experimental data points spaced by 0.05 decade of time are plotted. The calculated curves generally agree well with the

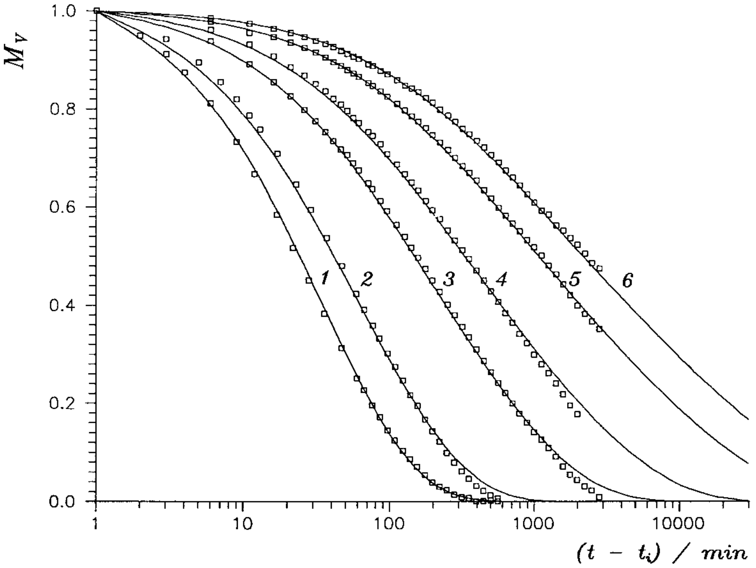

Fig. 11. Comparison of experimental relaxation data of As_2S_3 glass (□) and dependencies calculated using Eqs. (9)–(11) for TNM parameters (Table 1) at various temperatures: (1) 183.1, (2) 177.9, (3) 169.0, (4) 160.9, (5) 152.7, and (6) 148.0°C. The initial time t_i (=5 min) is the time estimated for thermal equilibration of the dilatometer following the cooling from T_0.

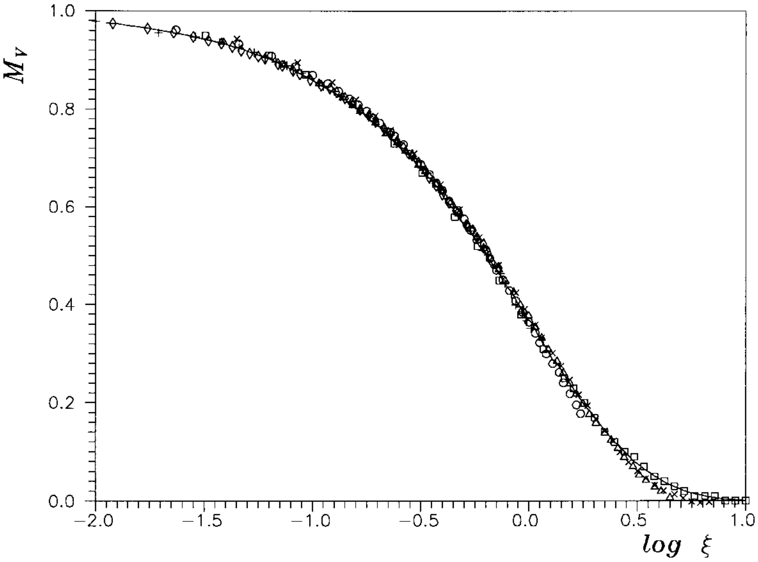

Fig. 12. Master relaxation curve for As_2S_3 glass. Solid curve was calculated using best fit parameters for the TNM model and symbols represent all data from Fig. 11: (×) 183.1, (△) 177.9, (○) 169.0, (+) 160.9, (◇) 152.7, and (□) 148.0°C.

data within the limits of experimental error. It is evident that these curves cannot be superposed by any linear shift in time axis. On the other hand, all experimental data can be directly compared in reduced time scale as shown in Fig. 12 where points represent all data from Fig. 11. The solid curve in Fig. 12 was calculated using Eq. (8) for the reduced time defined as

$$\xi = \sum_{\mathrm{i}=1}^{n} \frac{\Delta t_{\mathrm{i}}}{\tau_{\mathrm{i}}} \tag{17}$$

where the relaxation time τ_{i} in the subinterval Δt_{i} is calculated using Eqs. (9) and (10) for the TNM parameters shown in Table 1.

5. Discussion

The TNM model gives a good description of isothermal and isochronal structural relaxation data of As_2S_3 glass in the temperature range examined, i.e. up to 40°C below T_g. This phenomenological theory is based on the assumption of thermorheological simplicity (TRS) which means that the relaxation function $M_V(\xi)$ is identical at all temperatures because all the temperature dependence is included in reduced time ξ. The reduced time is defined by Eqs. (5) and (17) incorporating the temperature and the structure (i.e. the fictive temperature) dependence of the relaxation time τ. There are numerous experimental evidences that τ is linked with the viscosity [9,11]. Such link was also confirmed for our dilatometric measurement of structural relaxation of As_2S_3 glass, where the activation energy of structural relaxation time (Δh^*=269±4 kJ/mol) was found to be very close to the activation energy for temperature dependence of the equilibrium viscosity of undercooled liquid (E_η=267±9 kJ/mol).

The calculation of TMN parameters (i.e. β, x and ln A) is based on the assumption that the isothermal relaxation experiments correspond to temperature jump from T_g to annealing temperature T. It means that during previous cooling at −5 K/min the sample is cooled in equilibrium until the glass transition is reached and therefore the fictive temperature at the beginning of isothermal experiments is equal to T_g. In this case the equilibrium contraction Δ_∞ calculated using Eq. (2) should correspond to experimentally determined value. In fact, the experimental values of Δ_∞ as expressed by Eq. (15) are always higher than the values anticipated from Eq. (2) for instantaneous temperature jump. It seems, therefore, that some relaxation occurs during cooling from T_0 to T and also at the beginning of isothermal annealing before the initial time (t_{i}=5 min) is reached (see Section 3.2).

Comparison of master curve obtained from experimental data and calculated $M_V(\xi)$ function (see Fig. 12) reveals that there is a small but noticeable difference at longer reduced time particularly for lowest temperatures examined. This discrepancy could be eliminated assuming that the non-exponentiality parameter β is a weak function of temperature which would lead to the conclusion that TRS hypothesis is not valid for large temperature departures from T_g. It should be recognized, however, that TRS is an approximation applicable over a limited temperature range as was already discussed by Mazurin and Startsev [31] and Scherer [10]. The value of the non-exponentiality parameter found for the structural relaxation of As_2S_3 glass (β=0.82) suggests relatively narrow distribution of relaxation times in comparison with most polymers and some inorganic glasses [9].

Recently, Böhmer [32] proposed a relationship linking the non-linearity of structural relaxation with ‘fragility index’ m defined as

$$m = \frac{\Delta h^*/R}{2.303 T_g} \tag{18}$$

The concept of ‘strong’ and ‘fragile’ glass forming melts was originally suggested by Angell [33] and it associates ‘strong’ behavior with an Arrhenius temperature dependence of viscosity over a wide temperature range above T_g whereas ‘fragile’ behavior is defined as a marked departure from Arrhenius type dependence of log viscosity vs. reciprocal temperature plot. It was proposed that the degree of non-linearity, as expressed by the parameter x, exhibits an inverse correlation with the fragility index which has been examined in a wide range of both polymer and inorganic glasses [32].

The non-linearity parameter x, found by the curve-fitting technique for volume relaxation of As_2S_3 glass (x=0.31), is lower than the value 0.49 reported for enthalpy relaxation of As_2Se_3 glass [19]. Both these compounds form typical covalently bonded non-network glass forming liquid exhibiting similar fragility index defined by Eq. (18), i.e. m=31 for As_2S_3 (this work) and m=40 for As_2Se_3 glass [19]. The concept of linking of non-linearity of structural relaxation with strength and fragility of glass forming liquid would imply lower parameter x for As_2Se_3 glass than for As_2S_3 which is exactly the opposite than observed experimentally. Similar discrepancies were recently discussed by Hutchinson et al. [34] for the enthalpy relaxation in partially cured epoxy resin. It seems, therefore, that the link between the strength/fragility concept and non-linearity is not so clear when some specific glass forming systems are examined in detail.

It is interesting to discuss the stabilization period of structural relaxation defined as $\log(t_m/t_0)$. Recently, it was shown [35] that the temperature dependence of the stabilization period of structural relaxation can be expressed as a linear function of temperature with slope:

$$\frac{\mathrm{d}\log(t_\mathrm{m}/t_0)}{\mathrm{d}T} = -\frac{(1-x)\theta}{2.303} \tag{19}$$

Such behavior was experimentally confirmed for structural relaxation of As_2S_3 glass as shown in Fig. 10. When multiplied the slope of $\log(t_m/t_0)$ vs. T plot by $2.303/\theta$, this gives the value of x=0.31 which corresponds to the value obtained by curve fitting technique (see Table 1). Eq. (19) is useful for the estimation of temperature dependence of the stabilization period of various glass forming systems. It is seen that for a given value of x the temperature dependence of $\log(t_m/t_0)$ is controlled by the value of parameter θ. As noted in Section 2, the values of this parameter are similar for a wide variety of materials, generally being of the order of unity for polymers and 0.1–0.3 for inorganics [9]. Therefore, the stabilization period of structural relaxation of polymers can be expected to be ca. 10 times more temperature dependent than for inorganics, provided that the non-linearity is comparable. Such behavior is also experimentally observed [36,37].

6. Conclusions

The structural relaxation and viscosity of arsenic sulfide glass was studied by length dilatometry. It was found that the TNM model gives a good description of isothermal and isochronal dilatometric relaxation data of As_2S_3 glass in the temperature range up to 40°C below T_g. Small discrepancies observed for longer reduced time at lowest temperatures can be eliminated by introducing weak temperature dependence of the parameter β. Within the limits of experimental errors, the activation energy of relaxation process is identical with the activation energy of viscous flow in undercooled liquid near T_g (T_g=188°C for q_1=−5 K/min) and it was found to be Δh^*=267 kJ/mol. The non-linearity parameter (x=0.31) is considerably lower than the value reported for enthalpy relaxation of As_2Se_3 glass. On the other hand, the non-exponentiality parameter (β=0.82) is relatively high which probably corresponds to relatively narrow distribution of relaxation time in comparison with most polymers and some inorganic glasses. It is argued that these results are difficult to explain within the concept of linking of non-linearity with strength and fragility of glass forming liquids. The stabilization period of relaxation response decreases linearly with temperature. The slope of this relationship depends on parameter x and $\theta = \Delta h^*/RT_g^2$.

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