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**STRUCTURAL RELAXATION IN TERMS
OF TNM AND AGS MODELS**

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In this article the structural relaxation of non-crystalline materials was studied. The materials researched in this work were amorphous selenium, Ge_2Se_{98} , As_2Se_{98} , and poly(vinyl acetate). These materials were chosen due to their similar polymeric nature and also for being typical representatives of the respective groups of materials. Two types of relaxation – volumetric and enthalpic – were studied by using mercury dilatometry and differential scanning calorimetry. The relaxation of the materials studied was described on the basis of the Tool–Narayanaswamy–Moynihan (TNM) and Adam–Gibbs–Scherer (AGS) models. The main objective of this work was to describe and compare the volume and enthalpy relaxation of glassy Se, Ge_2Se_{98} , As_2Se_{98} and PVAc. It was found that in case of all these materials the apparent activation energy of the relaxation process, Δh^ , was similar for both the volume and enthalpy relaxation. Moreover, the value of Δh^* was found to be close to the activation energy of viscous flow, E_{η} , determined in the glass transition area. Approximate relations between the*

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volumetric and enthalpic as well as between the TNM and AGS model parameters were determined and applied to all the studied materials. Secondary objective of this article was to review and compare the results of non-fitting methods of the TNM parameters estimation with the results obtained from curve-fitting. Four non-fitting methods were tested — the inflectional analysis, the peak-shift method and the estimation of Δh^* from classic and intrinsic cycles. A good agreement between the estimates and curve-fitting results was obtained for all the materials studied; the only exception was the Δh^* evaluation from classic cycles which provided an inconsistently high value compared to that from curve-fitting.

Theory

In spite of the great importance of non-crystalline materials and long history of their examination, the very process of glass forming is still not fully understood and the true nature of the glass transition phenomenon remains unrecognized.

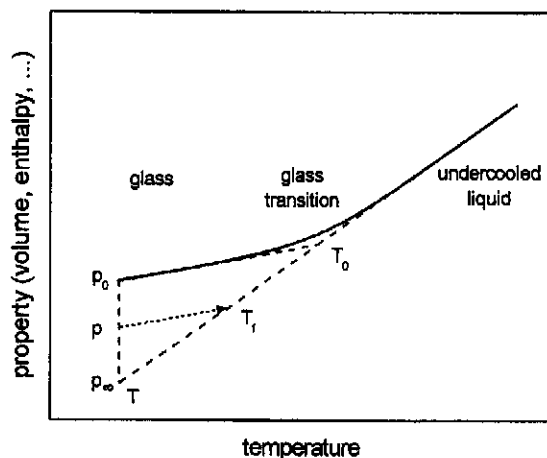


Fig. 1 Temperature dependence of a property (volume or enthalpy) relaxing at constant pressure. Index “0” represents initial state of the formed glass while index “ ∞ ” represents the equilibrium state of the material. Evaluation of the fictive temperature T_f is demonstrated

Glass transition is a widely studied phenomenon that can be shortly described as a process at which some macroscopic property (volume, enthalpy, refraction index ...) departs during continuing cooling from the undercooled liquid equilibrium state. The slope of the property-temperature curve decreases from its undercooled liquid value (higher temperature) to the glassy value (lower temperature). At that moment the glass is formed and the glass transition

temperature T_g can be evaluated as an intersection of the liquid and glassy asymptotes. Glass transition temperature is cooling rate dependent as the system departs from equilibrium due to the timescale for molecular motions becoming longer than the time available for these motions (which is determined by the cooling rate) [1]. In other words, at T_g the system can no longer achieve its structural equilibrium within the available time given by the rate of cooling. The non-equilibrium nature of the glassy state results in structural relaxation. This process (in polymer physics often called “physical aging”) occurs within and below the glass transition region and can be described as the spontaneous change of the structure towards its equilibrium state represented by the undercooled liquid extrapolation to the given temperature (Fig. 1). The rate at which the system approaches the equilibrium depends on actual temperature and structure (i.e. thermal history) of the glass [2]. Structural relaxation is often classified according to the property that is being observed — e.g., the volume or enthalpy relaxation.

It is a well-known fact that structural relaxation is a non-exponential and non-linear process. Non-exponentiality of the structural relaxation is often described by means of the distribution of relaxation times which is expressed by the Kohlrausch-Williams-Watts (KWW) stretched exponential function [3,4]. The KWW function is defined as follows

$$\Phi(t) = \exp(-\xi^\beta) = \exp\left[-\left(\int_0^t \frac{dt}{\tau}\right)^\beta\right] \quad (1)$$

where $\Phi(t)$ is the relaxation function, ξ is the reduced time, τ is the relaxation time which is a function of the temperature T and actual structure of the material, β is the parameter of non-exponentiality and is inversely related to the width of the relaxation times distribution ($0 \leq \beta \leq 1$).

The non-linear character of the structural relaxation is often described on the basis of Tool's concept [5] that the relaxation time depends on both temperature and actual structure of the material. This instantaneous structure of the system can be described by the fictive temperature, T_f introduced by Tool. The fictive temperature is defined as the temperature of the undercooled liquid which has the same structure as the relaxing glass (Fig. 1). Tool's concept was then modified by Narayanaswamy and Moynihan [6,7]

$$\tau(T, T_f) = A_{TNM} \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \quad (2)$$

where A_{TNM} is the preexponential factor (which stands for the relaxation time at an infinitely high temperature), x is the parameter of non-linearity which describes the

temperature/structure ratio of contribution to the relaxation time, $\Delta h^*/R$ is the apparent activation energy of structural relaxation; the meaning of other symbols is obvious or explained above. The set of equations (1) and (2) became known as the TNM (Tool–Narayanaswamy–Moynihan) model.

Another expression for the non-linearity of structural relaxation was presented by Scherer [8,9] who applied the Adam–Gibbs theory into the formulation of relaxation time. This concept was further improved by Hodge [10] and, together with Eq. (1), is known as the AGS (Adam–Gibbs–Scherer) model

$$\tau(T, T_f) = A_{AGS} \exp \left[\frac{B}{T \left(1 - \frac{T_2}{T_f} \right)} \right] \quad (3)$$

where A_{AGS} is the preexponential factor with similar meaning as that in the TNM model described above, B is a constant and T_2 represents the temperature at which the configurational entropy of the liquid would vanish. The temperature T_2 was found to be practically identical with the Kauzmann temperature T_K for some polymers. [11]

The TNM and AGS parameters can be evaluated either by the curve-fitting method or with the use of some non-fitting method based on the simple data analysis. Certain frequently used non-fitting methods are presented in the following text.

Dependence of T_g on Cooling Rate

An equation derived by Ritland [12] for the relation of the cooling rate and fictive temperature for glasses without memory effects was later extended by Moynihan *et al.* [7] for systems that exhibit a spectrum of relaxation times. Assuming the concept of thermorheological simplicity, i.e. that the distribution of relaxation times is temperature independent, the fictive temperature, T_f , obtained when a glass is cooled through the glass transition region, is shown [7] to be related to the cooling rate q^- by

$$\frac{d \ln |q^-|}{d(1/T_f)} = -\frac{\Delta h^*}{R} \quad (4)$$

where the fictive temperature T_f corresponds to the conventional T_g value obtained on cooling, i.e. to the temperature of intersection of the extrapolated liquid and glass property- T curves. Evaluation of the apparent activation energy $\Delta h^*/R$

according to Eq. (4) can easily be performed from the set of three-step DSC measurements. In such measurements first some short annealing at temperature well above T_g is applied to ensure that the sample is in thermal and structural equilibrium. Then the sample is cooled at a defined cooling rate q^- to some temperature well below T_g for the glass to be fully formed. After the sample is cooled immediate heating at q^+ to some temperature above T_g is applied. The previous thermal history is displayed during this heating scan in the endothermic peak at T_g (the so-called overshoot). The structure of the glass achieved during the cooling step (represented by T_p) can be evaluated using the “equal area method” [7,13]. This method is based on the following equation

$$\int_{T^*}^{T_f} (C_{pl} - C_{pg}) dT_f = \int_{T^*}^{T'} (C_p - C_{pg}) dT \quad (5)$$

where T^* is any temperature above T_g at which the heat capacity is equal to the equilibrium undercooled liquid value C_{pl} and T' is a temperature well below T_g where a constant value of C_{pg} was achieved. In order to evaluate $\Delta h^*/R$ from three-step measurements, various cooling rates together with constant heating rate have to be applied.

The same three-step cycles as described above can be used to estimate the non-exponentiality parameter β and/or non-linearity parameter x . [14] If the heating scan curves are normalized in order for C_p to rise from zero (glassy state) to unity (undercooled liquid state), then the C_p value of the maximum of the endothermic peak is denoted C_p^{max} . The comparison of experimental values of C_p^{max} determined for the set of cooling rates with theoretically modeled values for various combinations of β and x is then performed.

Peak-Shift Method

The peak-shift method [15,16] is a non-fitting method that provides an estimation of the non-linearity parameter x . This method was originally based on the Kovacs–Aklonis–Hutchinson–Ramos (KAHR) phenomenological model [17] for description of the structural relaxation. In this model the apparent activation energy was related to the temperature factor θ through the following equation

$$\theta \approx \frac{\Delta h^*}{RT_g^2} \quad (6)$$

Four-step thermal cycles are used in the peak-shift method. The first step is a short annealing at temperature well above T_g in order for the sample to achieve thermal

and structural equilibrium. The equilibrium annealing is followed by a cooling step at constant rate q^- to a temperature T below T_g where annealing for various periods of time t_a is applied. During this annealing the sample relaxes and changes its structure (fictive temperature) towards the equilibrium one. After a certain period of time the sample is immediately heated at a constant heating rate q^+ until equilibrium is established again at high temperature. The amount of relaxation proceeded during the previous annealing step is displayed during the heating scan as the overshoot effect at T_g . To quantify the degree of relaxation during annealing at T , the total excess enthalpy, δ_H , can be evaluated as

$$\delta_H = \Delta H - \Delta H_0 \quad (7)$$

where ΔH_0 is the equilibrium enthalpy achieved during the cycle with $t_a = 0$, and ΔH stands in this equation for the excess enthalpy achieved during the cycle when relaxation proceeded. Hutchinson and Ruddy [15,16] show that the maximum of the endothermic peak T_p displayed during the heating scan at T_g depends on experimental variables according to the following equations

$$s(Q^-) = \theta \left(\frac{\partial T_p}{\partial \ln |q^-|} \right)_{\delta_H, q^+} \quad (8)$$

$$s(D_H) = \Delta C_p \left(\frac{\partial T_p}{\partial \delta_H} \right)_{q^-, q^+} \quad (9)$$

$$s(Q^+) = \theta \left(\frac{\partial T_p}{\partial \ln |q^+|} \right)_{\delta_H, q^-} \quad (10)$$

where $s()$ stands for the peak shift of certain property; Q^- , D_H and Q^+ are the normalized dimensionless variables where $Q^- = \theta q^-$, $D_H = \theta \delta_H / \Delta C_p$ and $Q^+ = \theta q^+$. These shifts were evaluated under limiting conditions of a well-stabilized glass, i.e. of a glass that was annealed for a long time. The importance of this last statement lies in occurrence of the so-called “upper peak” [14] instead of the main annealing peak during the heating scan in the case of poorly stabilized glass (shorter annealing times). The difference between these two types of peaks lies in their dependence on experimental conditions as the temperature of the maximum of the upper peak T_u is almost independent of the amount of annealing δ_H . It was shown [18] for the main annealing peak that the shifts are inter-related

$$F(x) = s(D_H) = s(Q_2) - 1 = -s(Q_1) \quad (11)$$

The dependence of $F(x)$ on x can be expressed by the following equation

$$F(x) = x^{-1} - 1 \quad (12)$$

It can also be shown by theoretical simulations that the function $F(x)$ is markedly insensitive to the selection of relaxation times distribution. In practice the $F(x)$ function is evaluated from $s(D_H)$, i.e. from the experimentally determined dependence of T_p on δ_H .

It was further shown [14] from theories outlined above that the apparent activation energy of structural relaxation $\Delta h^*/R$ can be evaluated from three-step DSC experiments where the ratio of the cooling and heating rate remains the same (i.e. the heating rate is not constant as it was in similar experiments mentioned in the previous chapter but changes together with the cooling rate). The evaluation can be performed according to the following equation

$$-\frac{\Delta h^*}{R} = \left[\frac{d \ln |q^*|}{d(1/T_p)} \right]_{q^-/q^* = const} \quad (13)$$

where T_p is the temperature of the maximum of the endothermic relaxation peak.

Inflectional Analysis

Málek [19,20] performed a complex data analysis for isothermal down-jump relaxation experiments. The analysis is based on TNM equations, and the simulations of down-jump experiments under various conditions showed that TNM parameters can be evaluated from the dependence of the so-called “stabilization period” of the relaxation process on ΔT

$$\log \left(\frac{t_m}{t_0} \right) = \frac{1.18}{\beta} + \frac{(1-x)\theta}{2.303} \Delta T \quad (14)$$

where t_0 and t_m are intersections of the inflectional tangent with ordinates at one and zero in the ‘normalized property’/ $\log(t)$ plot, respectively. The expression $\log(t_m/t_0)$ is denoted as the stabilization period and is shown to be linearly dependent on the magnitude of the temperature jump ΔT under assumption of uniform T_0 for all down-jump relaxation curves. Furthermore, Málek [19] shows that both, t_0 and t_m increase linearly with ΔT and the parameters $\Delta h^*/R$ and x can be evaluated from these dependences according to equations

$$\frac{d \log(t_m)}{d \Delta T} \approx = \frac{\theta}{2.303} \quad (15)$$

$$\frac{d \log(t_0)}{d \Delta T} \approx = \frac{x \theta}{2.303} \quad (16)$$

where $\Delta h^*/R$ can be evaluated from θ according to Eq. (6). Equations (15) and (16) were derived assuming that the time t_m required to reach the equilibrium state is practically independent of the non-linearity effects due to the close proximity of the system to the equilibrium. On the other hand, the non-linearity effect greatly influences the time t_0 that characterizes the initial part of relaxation where the system starts to decrease linearly with $\log(t)$.

Experimental

The Se, Ge₂Se₉₈ and As₂Se₉₈ glasses were prepared from the pure elements (5N, Sigma Aldrich). The proper amounts of elements were, for each glass, accurately weighed into a fused silica ampoule, degassed and sealed afterwards. The batched ampoule was then annealed in the rocking furnace at the temperature of 350 °C for 24 hours. The glass was prepared from its melt by cooling the ampoule in air. The amorphous nature of the glass was checked by X-ray diffraction, homogeneity of the glass was verified from the position of the relaxation peak which was measured under defined thermal history for samples taken randomly from the bulk glass. PVAc studied in this work was the granular form of the Mowillith 50 (molecular weight $M_w = 260\ 000$). The very samples were from the materials studied prepared according to the method that was used to study the relaxation behavior.

Mercury dilatometry was used to study volume relaxation of the above mentioned materials. The dilatometers were prepared according to ASTM D864 [21]. Based on the comparison of relaxation results obtained for two differently constructed dilatometers with pure selenium, the optimum dilatometer proportions and sample/mercury volume ratio was chosen for the other studied materials. Capillaries were carefully chosen to have a constant diameter along their whole length and the angle between the capillary and the tube with specimen was approximately 80° to avoid blocking of the capillary by softening sample. The samples of chalcogenide glasses were in the form of cylindrical rods with the diameter of 6 mm. Due to the relatively low heat conductivity of PVAc, the original granules of this material were used directly as the sample instead of injection-moulding them into a thicker rod sample. Filled dilatometers were carefully checked not to contain any bubbles. The calibration of dilatometers was

performed at temperatures well above T_g to assure that the samples are not only in thermal but also in structural equilibrium. The value of the characteristic dilatometer time, t_i , was 70 s for the Se, $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$ dilatometers. The value of $t_i = 40$ s was determined in the case of PVAc. The volume relaxation measurements were carried out using three temperature-controlled water baths with an attached cooling device. The readings were taken manually using a magnifying lense; the overall sensitivity varied for individual dilatometers in the range $(4-15) \times 10^{-6} \text{ cm}^3 \text{ cm}^{-3}$.

The enthalpy relaxation of the materials studied was measured using the conventional DSC 822° (Mettler, Toledo) equipped with refrigerated cooling accessory. Dry nitrogen was used as the purge gas at a rate of $20 \text{ cm}^3 \text{ min}^{-1}$. The calorimeter was calibrated using the melting temperatures of In, Zn and Ga. Baseline was checked daily. The samples of chalcogenide glasses were in the form of powder. Thin layer of the powder was spread on the bottom of each aluminum pan to improve the thermal conduction; approximate mass of the samples was 8-9 mg. In the case of PVAc a thin layer of molten material had to be deposited on the bottom of the pans to improve the thermal conduction even more; the mass of each layer was approximately 6 mg.

Results and Discussion

This chapter will be divided into three parts. The curve-fitting results will be presented in the first part, the second part will treat the non-fitting methods of TNM parameters estimation and their comparison to those determined from curve-fitting and, finally, the third part will compare the relaxation results with viscous behavior of the respective materials.

Curve Fitting

The fitting program was created on the basis of TNM and AGS models. The input data were either in the form of the normalized relaxation function (isothermal experiments) or in the form of the normalized heat capacity (non-isothermal measurements) — Eqs. (17) and (18), respectively.

$$\Phi(t) = \frac{T_f(t) - T}{T_0 - T} \quad (17)$$

$$C_p^N = \frac{dT_f}{dT} = \frac{C_p - C_{pG}}{C_{pl} - C_{pG}} \quad (18)$$

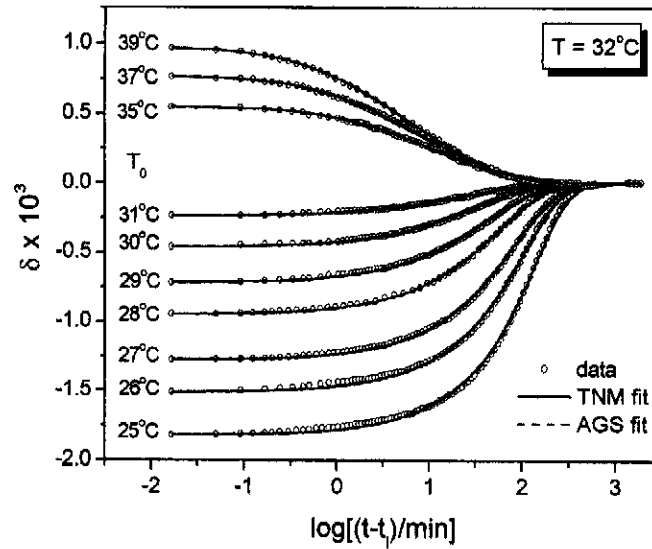


Fig. 2 The volume relaxation data corresponding to temperature down-jump and up-jump experiments for Se from different initial temperatures T_0 (indicated in figure) to the same final temperature $T = 32^\circ\text{C}$

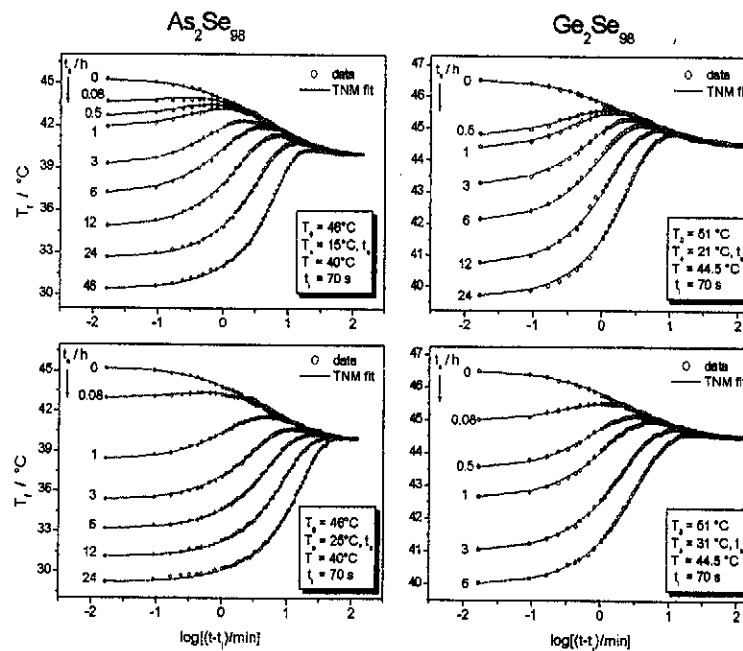


Fig. 3 Two sets of combined dilatometric experiments performed for $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$ glasses (particular thermal histories are presented in insets). Experimental data are fitted using TNM model

The fictive temperature was calculated according to the expressions from [22]. The parameters of a given model were obtained through a non-linear optimization method by using the Levenberg–Marquardt algorithm. The minimum of the residual sum of squares RSS was sought in order to obtain the best fit.

Large amount of experimental data was obtained for each of the studied materials in order to describe their relaxation behavior using the TNM and AGS models. Volume relaxation measurements included several sets of down-jump, up-jump and so called “combined” experiments. Especially the combined experiments (down-jump from temperature T_0 , annealing at temperature T_a for certain period of time — annealing time t_a — followed by temperature up-jump to a temperature T ; $T_a < T < T_0$) were essential for the correct and accurate determination of the TNM and AGS parameters, so at least two sets of these experiments were performed for each of the studied materials. In order to determine the enthalpy relaxation parameters, the curve-fitting procedure was for each material applied to several sets of various experiment types: the classic cycles (three-step cyclic experiments described in chapter *Dependence of T_g on cooling rate*), the intrinsic cycles (three-step cyclic experiments described at the end of chapter *Peak-shift method*) and the annealing experiments (four-step cyclic experiments described in chapter *Peak-shift method*). Examples of the fitted volume and enthalpy data are shown in Figs. 2-5. See the figure captions for details about particular measurements. The determined TNM and AGS parameters are summarized in Table I at the end of the chapter *Results and discussion*.

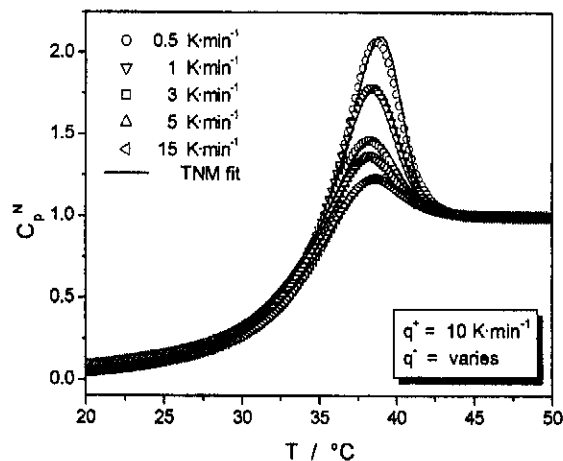


Fig. 4 Best fits of the normalized heat capacity C_p^N curves from enthalpic classic cycles performed on PVAc at heating rate 10 K min^{-1} following a cooling step at various cooling rates. The experimental data are fitted using TNM model

Comparing the volume and enthalpy relaxation described by TNM model, one can see that for all studied materials the apparent activation energy $\Delta h^*/R$ and pre-exponential factor A are similar for both types of relaxation, while the non-linearity parameter x and non-exponentiality parameter β are both notably higher in the case of enthalpy relaxation. The parameters x and β increased by an approximately analogous amount for all the materials. Moreover, similar relations were found between the volumetric TNM and AGS parameters for Se and PVAc — the same value of β for both models, T_2 being close to the Kauzmann [23] temperature T_K and a similar ratio of $\Delta h^*/B$ for both materials. If the $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$ relaxation parameters are compared to those for pure selenium, the following can be stated: the apparent activation energy of structural relaxation Δh^* is much higher for $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$ than for pure selenium; higher value of $\ln A$ for selenium alloys is primarily a consequence of the contrast between the values of Δh^* for the confronted materials; whereas the non-exponentiality parameter β remains the same (within the experimental error) for all the three glasses, the non-linearity parameter x is significantly higher for pure selenium.

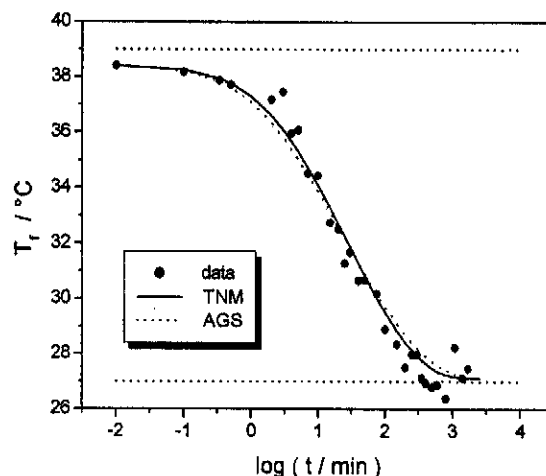


Fig. 5 Time evolution of the fictive temperature after the enthalpy down-jump; relaxation data are for Se ($T_0 = 39$ °C, $T = 27$ °C). Points correspond to experimental data. Solid line represents the TNM fit, broken line represents the AGS fit

Non-Fitting Methods

Besides the curve-fitting technique several other methods exist to determine or at least estimate the TNM relaxation parameters from volume or enthalpy measurements. The inflectional analysis, evaluation from intrinsic cycles and evaluation from classic cycles were applied to the experimental data to estimate

the apparent activation energy of structural relaxation Δh^* , the peak-shift method was applied in order to obtain the non-linearity parameter x .

The inflectional analysis proposed by Málek [19] and described in chapter *Inflectional analysis* is a simple but effective method of determining certain TNM parameters from a set of temperature down-jump experiments. Unfortunately, a lot of experimental techniques suffer from needing some kind of temperature stabilization prior to any isotherm that is following a temperature change. Due to this stabilization, the initial time t_0 of the isothermal relaxation is uncertain and can be determined only with large error. The only parameter that is independent of t_0 is the effective activation energy $\Delta h^*/R$. This parameter can be evaluated (Eq. (15)) only by use of equilibrium times t_m which can be determined accurately. The Δh^* evaluation together with the t_m determination is for the Se sample shown in Fig. 6.

The second method of $\Delta h^*/R$ estimation is based on Eq. (13) applied to the DSC intrinsic cycles (theory described in chapter *Peak-shift method*). Three sets of intrinsic cycles were performed for each material in order to obtain average value of T_p for each of the various applied cooling rates. Linear fit to the data plotted as a logarithm of cooling rate versus the maximum of the relaxation peak is shown in Fig. 7 for the case of $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$. It can be seen that the error of this measurement is very low as the maximum of the peak can be determined very accurately and any slight changes of experimental conditions that can influence the baseline or thermal gradients in the sample do not shift the value of T_p . It was further confirmed that for the given cooling and heating rate the value of T_p is independent of the concrete temperatures the sample was cooled from and to.

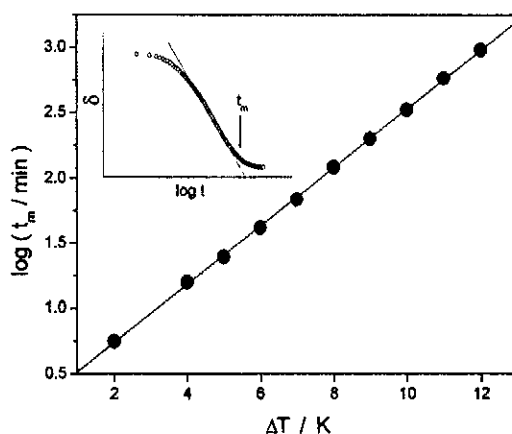


Fig. 6 Logarithm of t_m as a function of magnitude of temperature down-jump for volume relaxation data of Se (points). Solid line is a linear regression fit to these data. The inset shows the determination of t_m from experimental relaxation curve

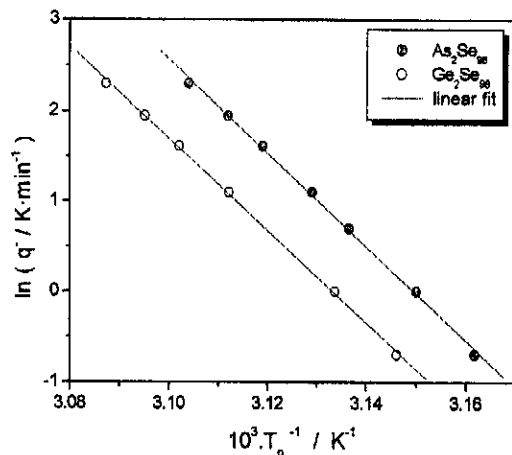


Fig. 7 Estimation of $\Delta h^*/R$ from enthalpic intrinsic cycles performed on $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$. Each experimental point is taken as a mean value of three measurements, experimental error of T_p evaluation is of the magnitude of the points. Linear fit of the data was applied in compliance with Eq. (13)

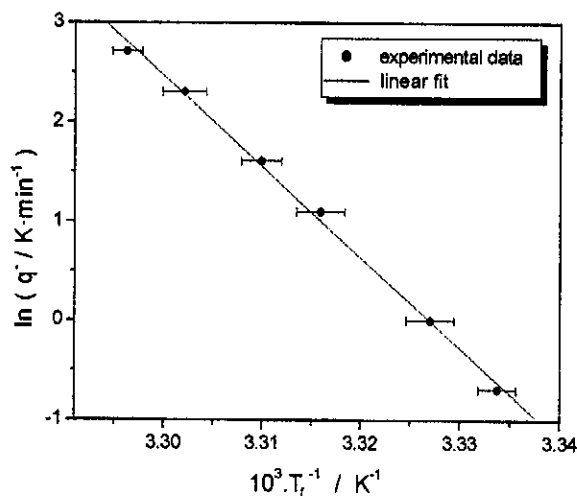


Fig.8 Estimation of the apparent activation energy of structural relaxation $\Delta h^*/R$ from enthalpic classic cycles measured for PVAc. Each experimental point is taken as a mean value of three measurements — linear fit of the data was applied in compliance with Eq. (4)

Finally, $\Delta h^*/R$ can be estimated from the dependence of T_g on cooling rate (chapter *Dependence of T_g on cooling rate*). Three sets of classic DSC cycles were performed for each material studied, the fictive temperature attained during the cooling step was determined by the equal area method according to Eq. (5). Example of the $\Delta h^*/R$ evaluation for PVAc is shown in Fig. 8. Errors displayed in

Fig. 8 are much higher than those of T_p measured during intrinsic cycles (Fig. 7). This is simply caused by the fact that fictive temperature is evaluated from the whole area under the experimental curve and even slight changes in height or width of the relaxation peak influence the resulting integral area significantly.

The estimation of non-linearity parameter x can be estimated on the basis of peak-shift method according to Eqs. (9), (11) and (12). In Fig. 9 an example of the dependence of the relaxation peak maximum T_p on excess enthalpy δ_H is shown for $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$. The annealing times (experiments described in chapter *Peak-shift method*) ranged from 0.5 to approximately 1400 minutes for each material; longer annealing times could not be applied due to the technical limitations. Short annealing times were applied in order to show the occurrence of upper peaks during experiments where only low amount of annealing is applied. This can be seen in Fig. 9 where main peaks started to occur for annealing times longer than approximately 3 hours. Slope of the dependence for the main peaks is suggested by the full line in the figure.

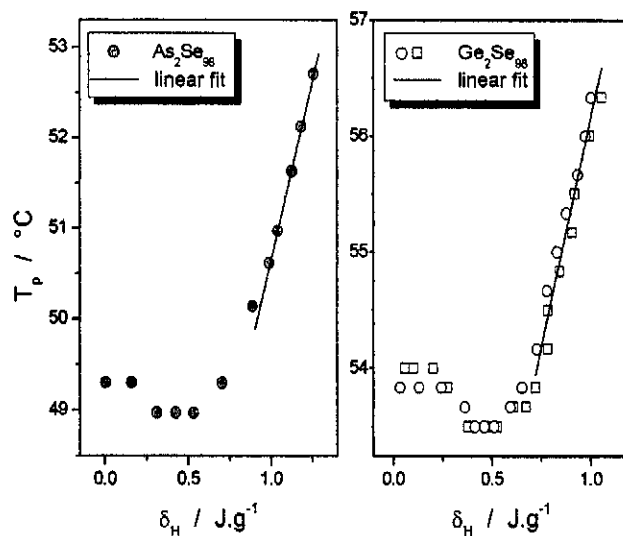


Fig. 9 Dependence of the maximum of the relaxation peak T_p on enthalpy loss δ_H during the annealing experiments performed on $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$. The annealing experiments performed on $\text{Ge}_2\text{Se}_{98}$ were performed in duplicate. Linear fit of the data was applied in compliance with Eq. (9)

Parameters x and β can be further evaluated from the classic cycles where experimental data are compared to the simulation of the dependence of the normalized relaxation peak height C_p^{max} on logarithm of the ratio of cooling rate to heating rate. Theoretical curves for several combinations of x and β together with experimental PVAc data obtained from classic cycles are depicted in Fig. 10; the values of the apparent activation energy $\Delta h^*/R$ and of the pre-exponential

factor A were taken from the curve-fitting results to calculate the theoretical curves. Comparison of experimental data with theoretical curves provides an estimate of the range within which the values of particular parameters can be localized. Only a rough estimate can be made in the case of both parameters being evaluated as curves for multiple combinations may fit the experimental data. On the other hand, if parameter x is already known (e.g. from the peak-shift method) the range for parameter β can be easily determined.

To summarize this chapter, one can say that the analysis of volumetric data proposed by Málek [19] together with the evaluation from intrinsic DSC cycles give, for all the materials studied, values of the activation energy of structural relaxation $\Delta h^*/R$ close to those determined from curve-fitting. On the other hand, the values of $\Delta h^*/R$ determined from classic cycles according to Eq. (4) are exceedingly high compared to the values from curve-fitting; a similar observation can be derived from results of Zumailan [24], Cortés *et al.* [25] and Echeverría *et al.* [26]. Furthermore, the peak-shift method and the simulation method both provide accurate and meaningful results but a careful analysis of the data has to be applied. The values of TNM and AGS parameters for all the non-fitting methods and materials are again summarized in Table I at the end of the chapter *Results and discussion.*

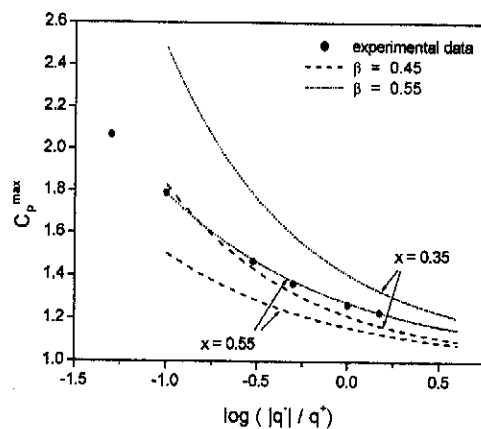


Fig. 10 Dependence of the normalized relaxation peak height C_p^{max} on $\log(|q|/q^*)$ for classic enthalpic cycles. The theoretical curves were calculated for $\beta = 0.45$ (dashed lines) and $\beta = 0.55$ (dotted lines), each with two different values of x (0.35 and 0.55). Points represent experimental data for PVAc

Viscous vs. Relaxation Behaviour

An interesting finding arises from the comparison of the apparent activation energy of structural relaxation, Δh^* , with the activation energy of viscous flow, E_{η} , determined in the glass transition range. It was found [27] that for many materials

these two values are similar, which confirms the idea of structural relaxation being the continuation of viscous flow. The same result was observed for the glassy selenium studied within the framework of this article. Viscosity data for amorphous selenium are introduced in Fig. 11 (the data were taken from literature [28-32]). As the evaluation of E_η is based on the Arrhenius-type equation, a proper temperature region has to be chosen for the determination of the dependence slope. This temperature region was chosen to correspond with the values of fictive temperatures reached by the samples during the relaxation experiments. This way determined value of E_η almost exactly matches the value of Δh^* obtained from relaxation measurements. Moreover, based on the data of Nemilov [33,34], Pustková *et al.* [35] and the data presented in this article, a similar trend in the compositional dependencies of Δh^* and E_η was found for both other chalcogenide systems, $\text{Ge}_x\text{Se}_{1-x}$ and $\text{As}_x\text{Se}_{1-x}$.

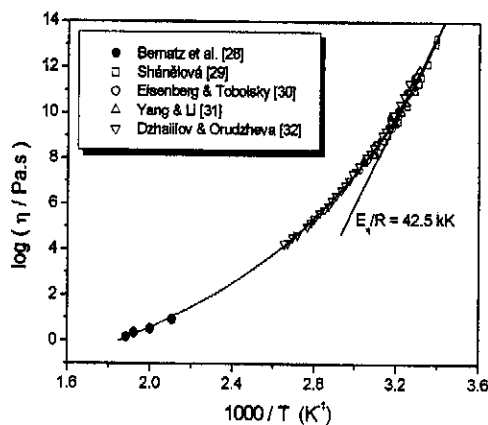


Fig. 11 The temperature dependence of the viscosity for Se supercooled liquid. The curve is best VFT fit to all experimental data. The straight line corresponds to the determination of the activation energy of viscous flow in the glass transition range

Conclusion

Structural relaxation of PVAc and Se, $\text{Ge}_2\text{Se}_{98}$ and $\text{As}_2\text{Se}_{98}$ glasses was studied by using mercury dilatometry and differential scanning calorimetry. The Tool–Narayanaswamy–Moynihan and Adam–Gibbs–Scherer models were used to describe the performed volumetric and enthalpic experiments. All of the measurements were fitted using a single set of volumetric and enthalpic TNM parameters that were determined for each studied non-crystalline material. Furthermore, a single set of volumetric and enthalpic AGS parameters was determined for PVAc and Se. Volume and enthalpy relaxations of all the materials

Table I Values of TNM and AGS parameters obtained by the best fit of enthalpy (H) and volume (V) relaxation data of Se, Ge₂Se₉₈, As₂Se₉₈ and PVAc. Abbreviations “infl.,” “intr.,” “class” and “p.s” denote results obtained from inflectional analysis, evaluation from intrinsic cycles, evaluation from classic cycles and results from peak-shift method, respectively

		Parameters of TNM model				Parameters of AGS model			
		$\Delta h^*/R$ kK	$\ln A$ s	x	β	B kK	$\ln A$ s	T_2	β
Se	V	42.8 ± 0.03	-133 ± 0.5	0.42 ± 0.05	0.58 ± 0.05	6.5 ± 0.5	-51 ± 3	190 ± 10	0.58 ± 0.05
	H	42.8 ± 0.03	-133 ± 0.5	0.52 ± 0.05	0.65 ± 0.05	6.5 ± 0.5	-57 ± 3	187 ± 7	0.65 ± 0.05
Ge ₂ Se ₉₈	V	50 ± 2	-153 ± 5	0.38 ± 0.05	0.56 ± 0.05	-	-	-	-
	H	50 ± 2	-152 ± 5	0.48 ± 0.05	0.62 ± 0.05	-	-	-	-
As ₂ Se ₉₈	V	52 ± 2	-160 ± 3	0.37 ± 0.05	0.60 ± 0.05	-	-	-	-
	H	52 ± 1	-158 ± 1	0.45 ± 0.05	0.63 ± 0.05	-	-	-	-
PVAc	V	55.6 ± 0.5	-177.5 ± 1.5	0.32 ± 0.05	0.46 ± 0.05	8.2 ± 0.2	-59 ± 3	174 ± 10	0.46 ± 0.05
	H	55.6 ± 0.5	-177.5 ± 1.5	0.43 ± 0.05	0.50 ± 0.05	8.2*	-70 ± 2	195 ± 4	0.47 ± 0.02
		infl.	intr.	class.	p.s.				
		$\Delta h^*/R$ kK	$\Delta h^*/R$ kK	$\Delta h^*/R$ kK	$\Delta h^*/R$ kK				
Se	V	47 ± 0.5	-	-	-				
	H	-	43 ± 1	54 ± 2	0.51 ± 0.02				
Ge ₂ Se ₉₈	V	52 ± 1	-	-	-				
	H	-	51 ± 1	87 ± 2	0.47 ± 0.01				

Table I — continued

		infl.	intr.	class.	p.s.
		$\Delta h^*/R$ kK	$\Delta h^*/R$ kK	$\Delta h^*/R$ kK	$\Delta h^*/R$ kK
As ₂ Se ₉₈	V	53 ± 1	-	-	-
	H	-	52 ± 1	89.5 ± 0.5	0.42 ± 0.01
PVAc	V	58 ± 1	-	-	-
	H	-	55 ± 2	91 ± 3	0.48 ± 0.04

* with parameter B held constant in the range of 6.5-8.5 kK equally good fits were obtained; set of AGS values was chosen for $B = 8.2$ kK (taken from volumetric measurements)

studied were compared on the basis of the TNM parameters values and the following conclusions were made. The apparent activation energy, $\Delta h^*/R$, and the pre-exponential factor, A , are the same for both types of relaxation while the non-linearity parameter x and the non-exponentiality parameter β were notably lower in the case of volume relaxation. The comparison of the activation energy of structural relaxation, Δh^* , and activation energy of viscous flow, E_m , was made for the available Se, Ge_{*x*}Se_{1-*x*} and As_{*x*}Se_{1-*x*} data. It was found that values of both, Δh^* and E_m are very close and follow the same trend in dependence on composition; and thus they confirm the idea of structural relaxation and viscosity being very closely related.

Furthermore, several methods of TNM parameters estimation were tested on the data presented. The estimation of $\Delta h^*/R$ was performed following three different methods — inflectional analysis, evaluation from intrinsic cycles and evaluation from classic cycles. A good agreement between estimates and curve-fitting results was achieved for all of the studied non-crystalline materials. Only the last-mentioned evaluation from classic cycles provided, in all the cases, a value of $\Delta h^*/R$ that was inconsistent with the results obtained from curve-fitting; which is, however, in the case of this method an occasionally observed issue. Furthermore, the peak-shift method and the simulation method have been applied on the enthalpy relaxation data in order to estimate parameters x and β . Both methods provided results that were for all the materials studied in a relatively good agreement with values obtained by curve-fitting.

Detailed results on PVAc and amorphous Se can be found in Refs [36] and [37], respectively.

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