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Fine kinetics of natural physical ageing in glassy $\text{As}_{10}\text{Se}_{90}$



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ABSTRACT

Sigmoid behavior of natural physical ageing in glassy $\text{As}_{10}\text{Se}_{90}$ reveals multi-step-wise growing kinetics of enthalpy losses. Phenomenological description of this kinetics can be adequately developed in terms of first-order relaxation processes, tending atomic structure from initial towards more thermodynamically equilibrium state. This kinetics is shown to obey characteristic stretched exponential behavior originated from a number of growing steps, attributed to the interconnected processes of chalcogen chain alignment and cooperative shrinkage of glass network.

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1. Introduction

Natural physical ageing (NPhA) effect occurring at well below glass transition temperature (T_g) is recorded for many network glass-formers, including oxide and chalcogenide glasses [1]. The nature of this effect is shown to be related to Johari–Goldstein (JG) β -relaxation [1]. Thus, structural data for Se-rich As–Se glasses suggest that NPhA is initiated by the elementary twisting of inner Se atoms within the specific double-well potentials (DWP) associated with high flexibility of chalcogen bonds [2–5]. In the first approximation, these twisted Se atoms (*cis-trans* re-conformations) can be accepted as elementary JG β -relaxation precursors. They should result in the appearance of aligned Se-based regions in a glassy network and, consequently, local free volumes released by twisted chalcogen atoms. Appearance of such free volumes around collapsed Se-based regions is assumed to be accompanied by elastic strains in their immediate atomic surrounding. This initial stage of NPhA is responsible for the lowering of T_g during the first period of NPhA [6]. If the accumulated elastic energy is high enough, the further cooperative rearrangements occur, eliminating redundant free volumes from the considered local atomic regions, which lead to the lowering internal energy of the system

at this particular scale. Happening at a larger scale, these relaxation processes should lead to general shrinkage of glass network. Therefore, in subsequent stages of NPhA, a general shrinkage of glassy network takes place, which can be attributed to JG β -relaxation facilitated α -relaxation events [3]. This process is a reason for increase in T_g and enthalpy losses ΔH in conventional differential scanning calorimetry (DSC) measurements for different aged Se-rich glasses [3,4,6].

2. Experimental

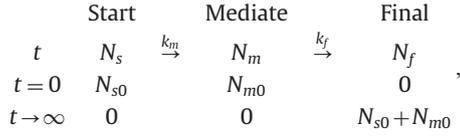
2.1. Kinetics modeling algorithm

Let us consider the process of twisting of Se atoms within DWP in $\text{As}_{10}\text{Se}_{90}$ glass, whose structure well satisfies the so-called “chain crossing” model that constitutes a uniform distribution of AsSe_3 pyramids interconnected by nearly equal Se chains [2]. Under such conditions, two possible DWP can be assumed for central Se atoms in $\text{As}_{10}\text{Se}_{90}$ composition owing to their immediate surroundings, namely –Se–Se–Se– and –As–Se–Se– fragments taken in 2:1 ratio. Obviously, these fragments differ by heights of energetic barriers separating DWPs properly into homopolar –Se–Se–Se– and heteropolar –As–Se–Se– environments. Owing to the magnitude of NPhA determined experimentally in Se-rich compositions of g-As–Se [7], the lower barrier for Se twisting can be ascribed to homoatomic, while the higher one to heteroatomic surrounding.

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Let us denote the relative probability of Se atom twisting within DWP as k_m and probability of further shrinkage as k_f . In the case of initial ($t=0$) nonzero population in the mediate state, the overall process of NPhA can be presented by the next scheme:



where N_s denotes the concentration of atomic sites described by DWP as precursors for Se twisting (N_{s0} is their initial concentration), N_m is the concentration of aligned Se chains as precursors for further atomic shrinkage (N_{m0} is their initial concentration), and N_f is the concentration of atomic sites affected by NPhA at the final stage of glass shrinkage ($N_{s0} + N_{m0}$ is the concentration of these sites, when NPhA is fully completed).

The inter-atomic balance between these start (s), mediate (m) and final (f) states can be determined as

$$N_s + N_m + N_f = N_{s0} + N_{m0} \quad (1)$$

Then, the set of first-order differential rate equations governing changes in the concentration of twisted (the mediate alignment stage) and densified (the final shrinkage stage) atomic sites can be composed for the considered network as follows:

$$\begin{cases} \frac{dN_m}{dt} = k_m N_s - k_f N_m \\ \frac{dN_f}{dt} = k_f N_m \end{cases} \quad (2)$$

The solutions of the above set of first order rates in Eq. (2) are

$$N_f = (N_{s0} + N_{m0}) \frac{k_f N_{s0} e^{-k_m t}}{k_f - k_m} + \left(\frac{k_m N_{s0}}{k_f - k_m} - N_{m0} \right) e^{-k_f t} \quad (3)$$

$$N_m = \frac{N_{s0} k_m}{k_f - k_m} e^{-k_m t} - \left(\frac{N_{s0} k_m}{k_f - k_m} - N_{m0} \right) e^{-k_f t} \quad (4)$$

Then, in accordance with the general principle that governs transition to structurally-dispersive media [8], the Kohlrausch relaxation function can be derived for NPhA kinetics from the above single-exponential expressions (3) and (4) by introducing the change of dimensionless variable

$$kt \rightarrow (kt)^\beta = \xi \quad (5)$$

where the fractional exponent $0 \leq \beta \leq 1$ is the so-called stretching parameter (also known as non-exponentiality or dispersivity index), ranging between 0 (high-dispersive processes) and 1 (single exponential relaxation) and the overall probability of NPhA connected with the same type of DWP is $k = k_m + k_f$.

Under such conditions, the differential rate equations (2) can be rewritten in the following form:

$$\begin{cases} k \frac{dN_m}{d\xi} = k_m N_s - k_f N_m \\ k \frac{dN_f}{d\xi} = k_f N_m \end{cases} \quad (6)$$

Solutions of these equations are

$$N_f = (N_{s0} + N_{m0}) \frac{k_f}{k_f - k_m} N_{s0} e^{-(t/\tau_m)^\beta} + \left(\frac{k_m}{k_f - k_m} N_{s0} - N_{m0} \right) e^{-(t/\tau_f)^\beta} \quad (7)$$

$$N_m = \frac{k_m}{k_f - k_m} N_{s0} e^{-(t/\tau_m)^\beta} - \left(\frac{k_m}{k_f - k_m} N_{s0} - N_{m0} \right) e^{-(t/\tau_f)^\beta} \quad (8)$$

where effective time constants of Se twisting within DWP and further atomic shrinkage can be defined as $\tau_m = k^{(1/\beta) - \beta} / k_m^{1/\beta}$ and $\tau_f = k^{(1/\beta) - \beta} / k_f^{1/\beta}$, respectively.

In such a way, we have obtained the dispersivity-related Master equation, which can be used to find the concentration of atomic

sites responsible for NPhA:

$$F = N_m + N_f = N_{m0} + N_{s0} \left(1 - e^{-(t/\tau_m)^\beta} \right) \quad (9)$$

All the parameters in Eq. (9) can be varied during fitting in order to obtain the best fit of the experimentally measured kinetics to the stretched-exponential law with $0 \leq \beta \leq 1$, minimizing the mean square-root deviation (improving goodness of fit, *err*). Eq. (9) can be also considered in terms of microstructural mechanism of NPhA developed for As–Se glasses [9], where two principally different possibilities are analyzed [10,11]:

- (1) the mechanisms happen once during the overall NPhA with k_m and k_f rates dependent on time (reflecting the statistical distribution of atomic sites involved into alignment-shrinkage process) and
- (2) the overall mechanism describing the process of NPhA relies on *routinely repeated relaxation stages*, when the final product of one process constitutes the initial stage for another within the newly formed glass network (*the serial processes*); or/and, alternatively, *the independent relaxation stages* with different k_m and k_f rates occur simultaneously (*the parallel processes*).

Another way to approach the dispersive-related relaxation is to assume that the corresponding kinetics originate from a weighted superposition of several separate contributions from elementary single-exponential Debye relaxation processes, as it was shown in Ref. [12] for decaying kinetics observed in the changes of refractive indices of some oxide glasses:

$$F(t) = F_1 e^{-t/\tau_1} + F_1 e^{-t/\tau_2} + \dots + F_n e^{-t/\tau_n} = \sum_{i=1}^n F_i e^{-t/\tau_i} \quad (10)$$

Such an assumption was frequently used in the past to interpret the dispersion of structural α -relaxation as superposition of exponential relaxation processes with different relaxation times τ_i weighed by F_i [12].

Eq. (10) describes the overall relaxation process in a glass as superposition of several single-exponential components, each of them being activated simultaneously (*the parallel processes*). Under the assumption that the mechanism describing NPhA is rather *the serial process*, the relaxation kinetics can be simulated by a sum of single exponential functions activated on different time scales:

$$F_i(t) = \sum_{i=1}^n \theta(t - \Delta t_i) \left[a_i + b_i \left(1 - \exp\left(-\frac{t - \Delta t_i}{\tau_i} \right) \right) \right] \quad (11)$$

where $\theta(t - \Delta t_i)$ is the Heaviside step function, whose value is accepted to be 0 for negative arguments ($t < \Delta t_i$) and 1 for positive ones ($t \geq \Delta t_i$), n is number of series in the overall relaxation process, b_i is the magnitude of i relaxation series, a_i is the sum of magnitudes of all previous relaxation series and Δt_i is the characteristic retardation time meaning the time shift between neighboring series.

Eqs. (10) and (11) can be considered as Master equations to describe NPhA consisting of several *parallel- and serial-type elementary relaxation events*, respectively, where each component is supposed to be a single-exponential. It can be noticed that Eq. (10) can be easily derived from Eq. (11) by setting the retardation times for each component to zero ($\Delta t_i = 0$). Therefore, Eq. (11) has a more general meaning, describing a full sum of *mixed serial-parallel relaxation events* depending on the fitting parameters used.

2.2. Samples preparation and experimental measuring procedure

The samples of glassy arsenoselenides exemplified by g-As₁₀Se₉₀ were selected to study NPhA kinetics. These samples obeying floppy chain-like structural fragments are more accessible to NPhA than

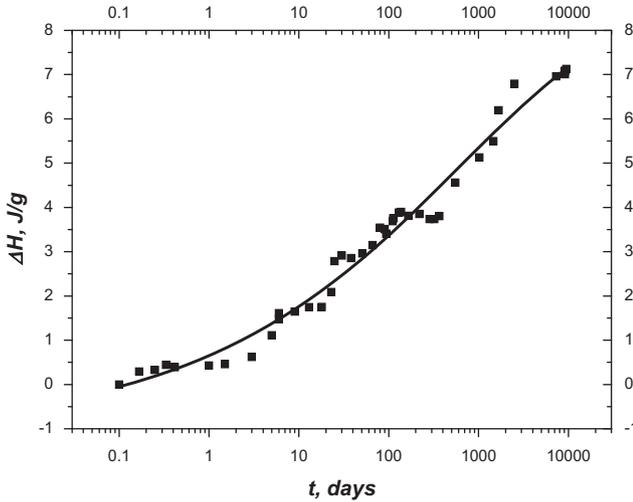


Fig. 1. Time-dependent enthalpy losses $\Delta H(t)$ in $g\text{-As}_{10}\text{Se}_{90}$ associated with long-term NPhA: the full squares correspond to experimental points; solid line is drawn in respect to the Master equation (9).

the branch-like ones near stoichiometric compositions [2,3]. They also have relatively high glass transition temperature (354 K in accordance to Refs. [2–4]) and, consequently, demonstrate strong peculiarities in kinetics behavior more pronounced than those in ageing of pure Se [3,4,6]. The studied $g\text{-As}_{10}\text{Se}_{90}$ samples were prepared by conventional melt-quenching route as described elsewhere [9]. Then, they were sealed in hermetic plastic bags and stored in dark under normal conditions for nearly two decades.

The DSC measurements were carried out using a NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC traces being recorded in the ambient atmosphere with $q=5$ K/min heating rate. More detailed description of the measurements protocol can be found in Ref. [9]. In short, the overall kinetics of time-dependent enthalpy losses $\Delta H(t)$ shown in Fig. 1 was obtained in a so-called *mixed backward-direct chronology*, when the final stage of NPhA was recorded in a backward chronology using a long-term aged sample and rejuvenation procedure, while the short-term stages were recorded in direct chronology during subsequent 6 years storage of the rejuvenated samples [9]. Experimental uncertainties in enthalpy losses $\Delta H(t)$ owing to incomplete rejuvenation affect only initial stages of NPhA without significant influence of the overall kinetics at the prolonged storage.

Fig. 1 represents the overall kinetics of enthalpy losses $\Delta H(t)$ in the studied $g\text{-As}_{10}\text{Se}_{90}$. The $\Delta H(t)$ kinetics curve exhibits clear plateaus and steep regions testifying non-elementary mechanism of physical ageing in $g\text{-As}_{10}\text{Se}_{90}$. Similar non-linearity in $\Delta H(t)$ was also observed previously for some other glasses [13] and polymers [14,15], but they were usually ignored during interpretation of the results and kinetics analysis. We believe just this circumstance may be a reason for discrepancy between timescales of NPhA in glasses reported by different authors.

Because of DSC-measuring uncertainties, the strict number of steps is difficult to determine unambiguously from a general view of this kinetics. Visually, the overall $\Delta H(t)$ curve can be approximated by five steps (within time intervals of 0–1.5, 1.5–20, 20–50, 50–365 and 365–9500 days), as it was suggested in Ref. [9] (see Fig. 2), or, alternatively, by four steps (within time intervals of 0–1.5, 1.5–20, 20–365 and 365–9500 days) (see Fig. 3). In the latter case, the third and fourth steps of the previous five-steps deconvolution are combined together.

The aim of this work is to analyze the overall kinetics of enthalpy losses $\Delta H(t)$ in $g\text{-As}_{10}\text{Se}_{90}$ (shown in Fig. 1) using

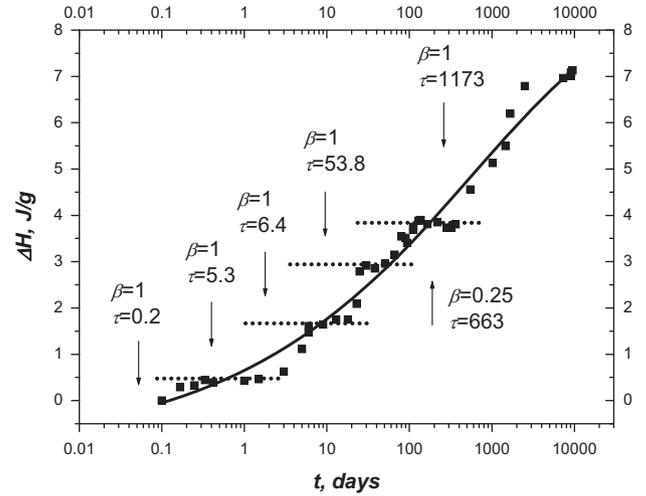


Fig. 2. NPhA kinetics in $g\text{-As}_{10}\text{Se}_{90}$ deconvoluted in five-steps serial single-exponential processes.

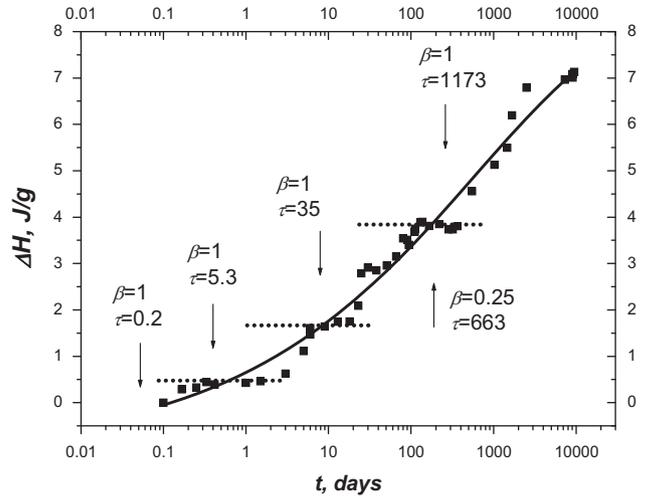


Fig. 3. NPhA kinetics in $g\text{-As}_{10}\text{Se}_{90}$ deconvoluted in four-steps serial single-exponential processes.

different possible approaches in respect to the developed Master equations (9)–(11). With a reasonable uncertainty proper to the conventional DSC technique and reliability of kinetics measuring within a quite long time periods, these modeling procedures allow β determination with a precision of not better than ± 0.05 .

3. Results and discussion

The straightforward fitting of the experimental data describing enthalpy losses $\Delta H(t)$ in $g\text{-As}_{10}\text{Se}_{90}$ during long-term NPhA with Eq. (9) gives $\tau_m = 7 \times 10^2$ days and $\beta = 0.25$ with a satisfactory high goodness of fit ~ 0.095 . In this case, the enthalpy losses $\Delta H(t)$ as described by Eq. (9) include nonzero initial concentration of atomic sites in the mediate state. If the population of atomic sites in the mediate state is zero ($N_{m0} = 0$), Eq. (9) can be further simplified as

$$F = N_{50} \left(1 - e^{-(t/\tau_m)^\beta} \right) \quad (12)$$

Results of $\Delta H(t)$ fitting with Eq. (12) for NPhA in $g\text{-As}_{10}\text{Se}_{90}$ (shown in Fig. 1) testify lower τ_m ($\sim 5 \times 10^2$ days) and higher β (~ 0.35) than with Eq. (9), but the goodness of fit is also worse

Table 1
Fitting parameters in Eq. (10) describing NPhA kinetics in g-As₁₀Se₉₀ as independent parallel relaxation stages.

Number of exponents	err	F _i (J/g)	τ _i (days)
1	0.710	F ₁ =7.1	τ ₁ =180.2
2	0.067	F ₁ =3.2; F ₂ =3.9	τ ₁ =15.1; τ ₂ =1356.7
3	0.048	F ₁ =3.8; F ₂ =2.6; F ₃ =0.8	τ ₁ =1445.8; τ ₂ =24.9; τ ₃ =1.7
4	0.062	F ₁ =1.8; F ₂ =2.2; F ₃ =1.5; F ₄ =1.6	τ ₁ =7.5; τ ₂ =1478.1; τ ₃ =31.0; τ ₄ =1335.0
5	0.061	F ₁ =0.9; F ₂ =0.9; F ₃ =0.8; F ₄ =0.8; F ₅ =3.8	τ ₁ =40.7; τ ₂ =27.9; τ ₃ =4.3; τ ₄ =6.5; τ ₅ =1433.2

Table 2
Fitting parameters in Eq. (11) describing five-step kinetics of NPhA in g-As₁₀Se₉₀.

Step number, duration (days)	err	r ²	a _i (J/g)	b _i (J/g)	τ (days)	Δt _i (days)
i=1 (0–1.5)	0.008	0	0.46	0.2	0	0
i=2 (1.5–20)	0.022	0.46	1.52	5.3	1.7	1.7
i=3 (20–50)	0.058	1.98	1.01	6.4	19.6	19.6
i=4 (50–365)	0.010	2.99	0.85	53.8	32.1	32.1
i=5 (365–9500)	0.034	3.84	3.27	1173	340	340

Table 3
Fitting parameters of Eq. (11) describing four-step kinetics of NPhA in g-As₁₀Se₉₀.

Step number, duration (days)	err	r ²	a _i (J/g)	b _i (J/g)	τ (days)	Δt _i (days)
i=1 (0–1.5)	0.008	0	0.46	0.2	0	0
i=2 (1.5–20)	0.022	0.46	1.52	5.3	1.7	1.7
i=3 (20–365)	0.038	1.98	1.82	35.0	16.5	16.5
i=4 (365–9500)	0.034	3.80	3.27	1173	340	340

(~0.115). This is due to evident changes in the curvature of the overall modeling function in the vicinity of starting point ($t=0$).

The parameters obtained from modeling of the overall NPhA kinetics for g-As₁₀Se₉₀ with Eq. (10), which assumes independent parallel relaxation processes, are given in Table 1.

As expected, the simple single-exponential presentation was not enough for the fitting of the overall kinetics, giving too low goodness of fit ($err=0.710$). However, sum of the two single exponents, which represents the overall NPhA process as two steps having saturation amplitudes 3.2 and 3.9 J/g with significantly different time constants ~15 and ~1357 days, respectively, already gives much better goodness of fit ($err=0.067$). Three-exponent presentation of parallel kinetics further improves the fitting, especially for the fast stages of NPhA owing to additional single-exponential component with ~2 days time constant. Further increase in the number of exponents, like four- or five-exponent presentations, did not improve the goodness of fit significantly, being within $err=0.061$ – 0.062 interval. Yet, the high goodness of fit with a number of single exponents should not be taken too optimistically in respect to the previous stretched exponential fit with Eqs. (9) and (12), since the number of fitting parameters used in Eq. (10) is higher too (related to the number of individual exponents used).

An interesting result can be obtained under the assumption of series processes in NPhA based on the hierarchically constrained relaxation dynamics [10]. This model involves a number of constraints (it should be noted here, that interactions between any chosen set of atoms are primarily restricted by the constraints) as well as the hierarchy of degrees of freedom, which govern the overall kinetics. In this case, Eq. (11) can be used to describe each step in NPhA through the sequence of single-exponential processes shifted by different retardation times Δt_i . The results of the modeling with Eq. (11) and the fitting parameters for five- and four-step serial presentation of NPhA are shown in Figs. 2 and 3 and Tables 2 and 3, respectively.

As can be evidently seen from Fig. 2 and Table 2, in the case of five-steps $\Delta H(t)$ kinetics, the observed gradual increases in τ_i parameters (from 0.2 to 1173 days) do not correlate with the trend in the magnitude of each relaxation component, which demonstrates overshoot for the second step, smaller values for the third and fourth steps and again increase for the last fifth step.

If $\Delta H(t)$ curve is divided into four steps (Fig. 3), all fitting parameters (τ , b_i and Δt_i) demonstrate strong increase with NPhA duration or step number (Table 3). Thus, if we accept four steps in the kinetics of NPhA in g-As₁₀Se₉₀, the observed behavior of fitting

parameters correlates well with the expected increase in cooperativity of the overall relaxation process [16].

Coming back to the model of NPhA in Se-rich g-As-Se, which explores the idea on Se atoms twisting within two kinds of DWP related to –Se–Se–Se– and –As–Se–Se– chemical environments [4], we expect these structural fragments to serve as real precursors for glass network shrinkage. The ageing dynamics for each chemical environment exhibits two-step scenario like in suspensions [16], where the faster relaxation events are initiated by single-particle motions (responsible for aligning of neighbored Se chains) described by a single exponential kinetics, while the slower relaxation events are based on many-particle cooperative process (glass shrinkage) which is stretched exponentially. These fast and slow relaxation stages are strongly hierarchically arranged for each atomic precursor (the slower processes start after the faster ones are completed) within the glass network (serial processes). We believe these hierarchically dependent processes have different effective time-constants and dispersivities as initiated by Se–Se–Se or Se–Se–As precursors, forming more or less independent channels of structural relaxation. The input from these channels to the overall NPhA kinetics in g-As₁₀Se₉₀ can be considered as parallel processes with different effective time constants. These serial and parallel two-step relaxation processes are strongly overlapped in real dynamics of long-term NPhA, and can result in a number of steps in the overall kinetics function. The intermediate steps in the NPhA kinetics are the result of complicated superposition of the individual time-dependent stages originated from both –Se–Se–Se– and –As–Se–Se– precursors. As a result, a clear step-wise behavior is observed in the enthalpy relaxation as recorded by DSC (Fig. 3), being a mix of serial-parallel processes.

The number of single-exponential steps in the observed NPhA kinetics for g-As₁₀Se₉₀ remains discussible. Obviously, there is a dependence on the number of –Se–Se–Se– and –As–Se–Se– precursors in a glassy network, which is determined by the glass composition. Some additional steps can arise also from a non-zero correlation between the parallel processes, like, for example, the relaxed structure as initiated by –Se–Se–Se– precursors can accelerate relaxation processes initiated by –As–Se–Se– precursors.

Despite the fact that each individual step can be described by a single exponential function, the overall process of long-term NPhA in ChG seems to be stretched exponentially. This is true, however, if the complete kinetics is studied, like in the present studies for g-As₁₀Se₉₀. Indeed, the fictive temperature in long-term aged samples of g-As₁₀Se₉₀ is close to room temperature (temperature of storage) [4], indicating almost completed NPhA in this glass after two decades of storage. This is important, since excluding the long-term components from consideration will lead to high values of β . Thus, for

example, if we exclude the last extended growing step in NPhA kinetics of g-As₁₀Se₉₀ (step 5 in Fig. 2 or step 4 in Fig. 3) from consideration, the obtained parameters from modeling are only $\tau_m=25\text{--}26$ days, $\beta=0.70$ and $\beta=0.65$ for Eqs. (9) and (12), respectively.

4. Conclusions

It was shown that kinetics of enthalpy losses $\Delta H(t)$ caused by prolonged storage of g-As₁₀Se₉₀ in dark at room temperature (natural physical ageing) for more than two decades, exhibits a well-expressed step-wise character, showing some kinds of plateaus and steep regions. The microstructural mechanism of natural physical ageing explains well the observed stretch-exponential behavior in relaxation kinetics in terms of hierarchically-constrained *mixed serial-parallel* relaxation events having different atomic precursors. This kinetics can be decomposed into elementary components, each of them being single exponential.

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