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Low-dimensional deterministic chaos in thermally-induced physical aging of $As_{10}Se_{90}$ glass probed with nonlinear time-series method

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Abstract. Nonlinear time-series method with the help of the TISEAN Program is applied to study the chaotic behavior in physical aging of $As_{10}Se_{90}$ glass accelerated with thermal annealing at 40 ^{o}C. The kinetics of enthalpy losses was measured experimentally to determine the phase space reconstruction parameters, the results being presented in terms of a comparison with naturally long-term aged glass of the same composition. The observed deterministic chaoticity (involving chaos and fractal analysis tools such as detrended fluctuation analysis, attractor identification using phase space representation, delay coordinates, mutual information, false nearest neighbors) is parameterized so as to compare with microstructural models of long-term natural (more than 2 decades) and light-assisted physical aging in As-Se glasses.
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1. Introduction

Being permanently in a metastable state because of frozen molten disordering, glasses can be subjected to a variety of external influences reducing their excess of configurational entropy, enthalpy or free volume [1]. This ability to stabilize a more energetically favorable structure is referred to as physical aging (PhA) [1-7], the phenomenon approaching temporal state of linearly extrapolated equilibrium of super-cooled liquid. Thus, natural and light-assisted physical aging in glassy arsenic selenides As-Se occurred to be essentially similar, demonstrating a number of common features [4]. The theory of strange attractors involving typical chaoticity considerations (such as detrended fluctuation analysis, attractor identification using phase space representation, delay coordinates, mutual information, false nearest neighbors, etc.) was adequately applied to describe multistep growing tendencies in both kinetics despite principally different time scales, tens of years for natural [4-7] and tens of days for light-assisted PhA [8-11]. It was proved that photoexposure could be as an initiating factor at the beginning stage of PhA, thus facilitating further atomic shrinkage of a glassy backbone at more prolonged time scales [11].

In contrast, the PhA can be also accelerated in other way by eliminating some mechanical constraints limiting atomic movements in a glassy network. This can be achieved due to allowing PhA at elevated temperatures, the process being known as thermally-induced PhA [4,12]. Nevertheless, there is an open question left in this connection: Does thermal influence affect PhA like photoexposure, causing deterministic chaoticity in the finalized kinetics?

In this work, we tried to answer this question by comparing natural and thermally-induced PhA behavior in glassy g-$As_{10}Se_{90}$, reconstructed with time series analysis [13,14] using TISEAN software program package [15].

2. Experimental Results

The samples of g-$As_{10}Se_{90}$ were prepared by conventional melt quenching route from a mixture of high purity precursors, as described elsewhere [4-6]. The kinetics behavior under natural (room temperature) and thermal storage (keeping in a furnace under 40 ^{o}C) was studied for bulk glassy ingots (~3 mm), which were preliminary subjected to rejuvenation by heating above glass transition temperature T_g ~350 K to erase any thermal prehistory.

PhA was tested with a differential scanning calorimetry (DSC) due to strong endothermic peak superimposed on the endothermic step of glass transition [16-18]. The DSC traces were recorded on NETZSCH 404/3/F set-up pre-calibrated with standard elements, all measurements being performed in a dark at ambient atmosphere with constant 5 K/min heating rate. The same calibration procedure was repeated each time during routine kinetics experiments. Three independent DSC scans were detected to confirm the reproducibility of results. Finally, the raw DSC data were processed using NETZSCH PC software package. The difference in the area under DSC signal from aged and rejuvenated glasses was

directly proportional to the enthalpy losses ΔH. In further, we will focus only on this parameter to describe the corresponding aging kinetics.
The aim of this paper is to provide a comparative study of chaotic behavior in g-$As_{10}Se_{90}$, affected by two principally different PhA scenarios at long- and short-term time scales, these being known as natural and thermally-induced PhAs.

3. Results and Discussion

The graphs of real time-dependent enthalpy losses $\Delta H(t)$ in g-$As_{10}Se_{90}$ ascribed to long-term natural PhA as given previously in [7], and activated by thermal influence at 40 ^{o}C are shown on Fig. 1 (top and bottom graphs, respectively).
As it follows from Fig. 1 (the top graph), the natural PhA exhibits well-expressed multi-step-wise kinetics, where four or five steps [6] can be distinguished in dependence on well-separated growing slope-plateau domains. Each such domain can be roughly substituted by elementary single-exponential component with time constants growing with aging duration in a sequence of 0.2-6-26-78-1529 days. Straightforward fitting of overall experimental curve describing enthalpy losses $\Delta H(t)$ in g-$As_{10}Se_{90}$ by stretched-exponential function gives numerical values of relaxation time $\tau \cong 663$ days and dimensionless stretching exponent (or non-exponentionality index) $\beta = 0.25$ [4-6].
In an obvious contrast, the kinetics of thermally-activated PhA (Fig. 1, the bottom graph) is smoother with only a few steps visible in growing $\Delta H(t)$ dependence (only two of them can be parameterized by single-exponential relaxation time constants of 5.7 and 195 hours), the overall relaxation process tending towards saturation just after ~10^3 hours. Straightforward stretched-exponential fitting of this kinetics curve proceeds with non-exponentionality index $\beta = 0.44$ and correspondingly shorter time constant $\tau \cong 114$ hours.
These irregular transient enthalpy $\Delta H(t)$ characteristics split into equal time domains (bins) by dividing on 10000 steps were taken as initial data for further non-linear time series analysis [15]. Hence, despite the same number of bins, the averaged weight of each bin was different for natural and thermally-induced PhA. Furthermore, we tried to reconstruct the best possible attractor responsible for this relaxation kinetics, the methods of time delay and false nearest neighbors being utilized [13,14]. After attractor reconstruction, we performed a determinism test by calculating the Lyaponov exponent. In such a way, we obtained strong indication on chaotic behavior of the tested relaxation kinetics affected by the reconstructed attractor, provided the calculated value of the largest Lyaponov exponent occurs to be positive [14].
Mutual information dependence on delay times for g-$As_{10}Se_{90}$ affected to long-term natural and thermally-activated (40 ^{o}C) PhA are shown respectively by green and red curves on Fig. 2. Within the TISEAN program [15], the value of time delay where mutual information reaches its first minimum was used for space reconstruction.
According to mutual information calculations, these delay times are nearly 250 and 150 time steps for naturally and thermally-aged g-$As_{10}Se_{90}$ because of the

same primary chemical environment affected by relaxation. Slight shortening in delay times for thermally-activated process probably originates from partially uncompleted aging kinetics in this case with preference of more flexible homoatomic Se-Se-Se configurations affected by relaxation, which stretches on principally another (more shortened) time scale.

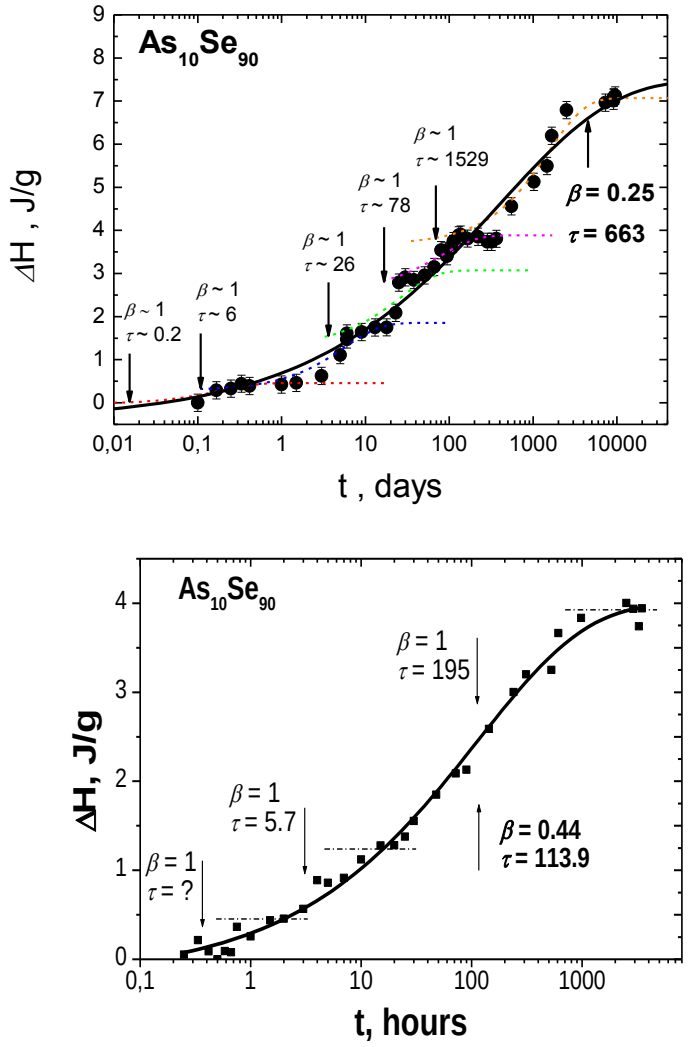

Fig. 1. Kinetics of DSC enthalpy *ΔH(t)* losses in g-$As_{10}Se_{90}$ subjected to long-term natural (top) and thermally-activated (40 ^{o}C) PhA (bottom).

After choosing an acceptable time delay *t*, we need an appropriate embedding dimension *m* to reconstruct the phase space correctly in order to avoid projecting the system onto a lower dimensional space. The approach known as false nearest neighbors (FNN) is useful to give such estimate for embedding dimension *m* [7, 11, 19, 20].

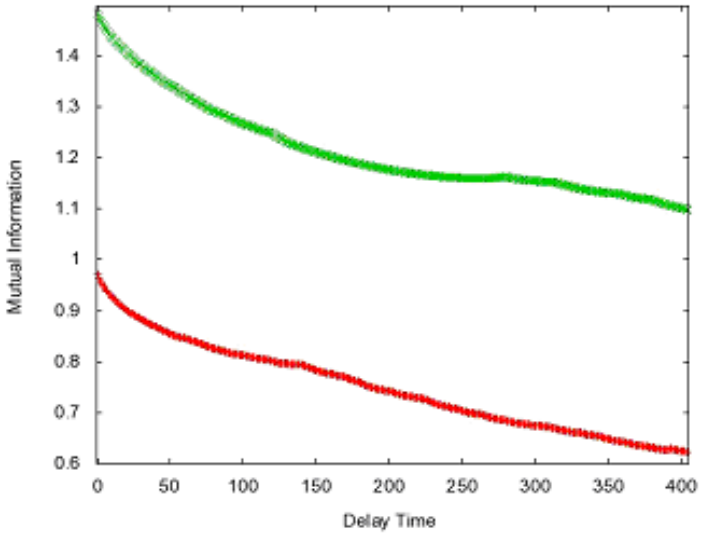

Fig. 2. Average mutual information *vs.* delay time graphs for g-$As_{10}Se_{90}$ affected to long-term natural (green curve) and thermally-activated PhA (red curve).

By taking the delay time as given above, we analyzed the minimum embedding dimension *m* needed to reconstruct attractor by this method for naturally and thermally-aged (40^{o}C) g-$As_{10}Se_{90}$ (green and red curves on Fig. 3, respectively).

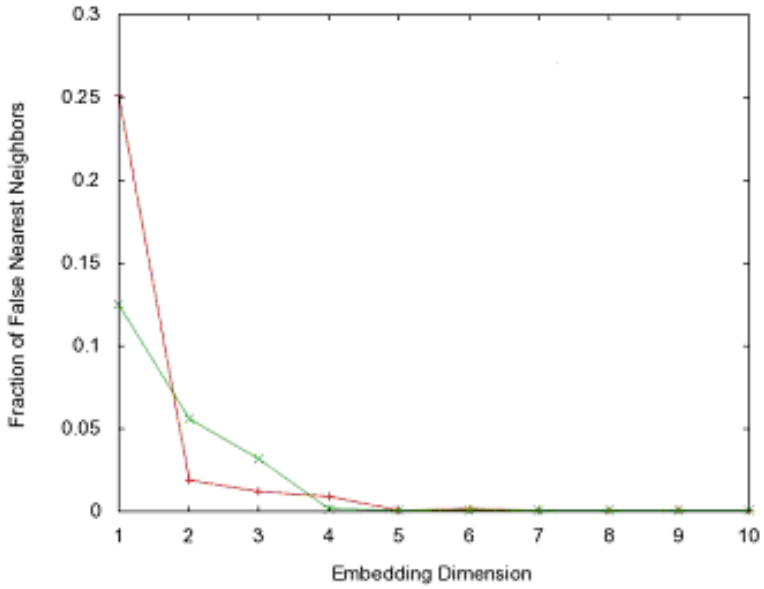

Fig. 3. Fraction of FNN *vs.* embedding dimension graphs for g-$As_{10}Se_{90}$ affected to long-term natural (green curve) and thermally-activated PhA (red curve).

In both cases, the PhA tends towards m=5 since the same chemical environment are involved in the respective structural-relaxation transformations. However, the starting stages of relaxation are more pronounced for thermally-induced PhA, thus producing long decaying "tail" in the number of FNN to m=5. Similar incompleteness at final stages of structural relaxation was also proper to light-assisted PhA in this glass caused by low-energy photons [11].

Having built an attractor, we should further clarify the system's behavior in a reconstructed phase space employing the scaling analysis of power-low correlation exponent [13-15]. In our research, to analyze short- and long-range correlations in the studied PhA kinetics, the method of detrended fluctuation analysis (DFA) was applied [15]. According to this DFA analysis (see Fig. 4), the starting stages of natural PhA in g-$As_{10}Se_{90}$ demonstrate the slope of ~1.6, changing it on ~1.9 with further stages, while this slope in nearly the same (close to ~1.6) for thermally-induced PhA. Since crossover in a scaling type of the underlying correlation can be attributed to transition in the dynamical properties of a system [13,14], we suppose some changes in this dynamics for natural and thermally-induced PhA in g-$As_{10}Se_{90}$. The starting stage of natural PhA in g-$As_{10}Se_{90}$ is governed mainly by Se atom twisting within double-well potentials formed by homopolar Se-Se-Se environment, while heteropolar Se-Se-As environment dominates in the final stage [4]. In contrast, the thermally-induced PhA in g-$As_{10}Se_{90}$ is stretched as a unique process with a full domination over entire time scales, originated exclusively from more easily affected homopolar Se-Se-Se environment (thermal treatment does not affect

more rigid heteropolar Se-Se-As environment, leaving a whole relaxation process uncompleted at such short durations).

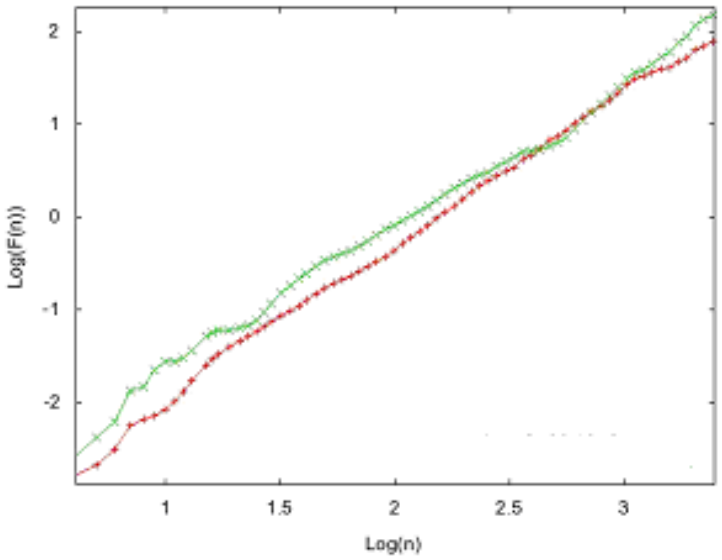

Fig. 4. DFA graphs for g-$As_{10}Se_{90}$ affected to long-term natural (green curve) and thermally-activated (40 ^{o}C) PhA (red curve).

To separate non-Gaussian signals from Gaussian ones in the reconstructed PhA kinetics (thus giving a predictability of time series), the rescaled range analysis was applied [13]. Using standard approach [13,15,20], we calculated the Hurst exponent *H* for both PhA processes as shown in Fig. 5. Two regimes with *H*=0.4 and 0.3 were detected, but not any difference between natural and thermally-induced PhA. The Hurst exponent in this domain (0-0.5) implies non-random behavior in a time series, which probably originates from non-randomness because of preferential chemical ordering in the studied glasses [4]. Both natural and thermal PhA in g-$As_{10}Se_{90}$ originates from Se atoms twisting within double-well potentials of the same environment, competitive channels being caused by 2/3 occupation of homopolar Se-Se-Se sites and 1/3 occupation of heteropolar Se-Se-As sites (thus resulting in two-regime R/S-Hurst behavior).

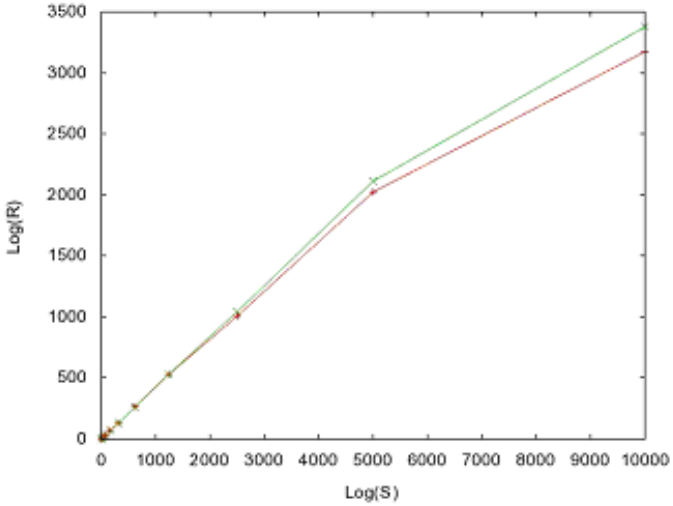

Fig. 5. Rescaled-range Hurst graphs for g-$As_{10}Se_{90}$ affected to long-term natural (green curve) and thermally-activated (40 ^{o}C) PhA (red curve).

4. Conclusions

The chaotic behavior in PhA of g-$As_{10}Se_{90}$ accelerated by thermal annealing at 40 ^{o}C was studied directly from experimental calorimetric data on real-time kinetics of enthalpy losses and compared with long-term natural PhA in the same sample. Chaoticity in natural and thermally-activated PhA can be attributed to complex structural-relaxation transformations evolving multiply-repeated cycles of Se atoms twisting within nearest chain environment.

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