PHYSICAL AGING

in nanostructured topologically disordered networks

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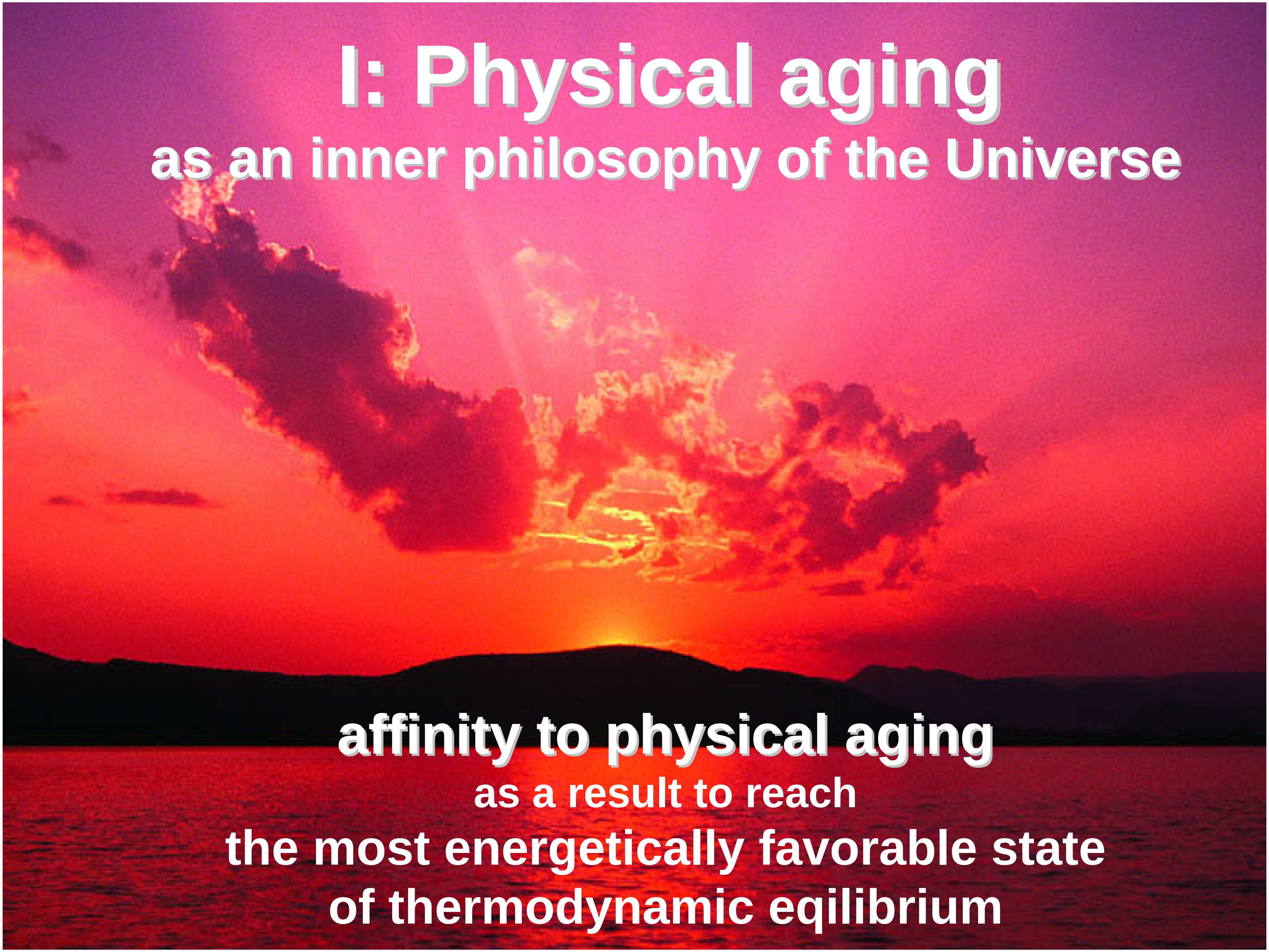
Content:

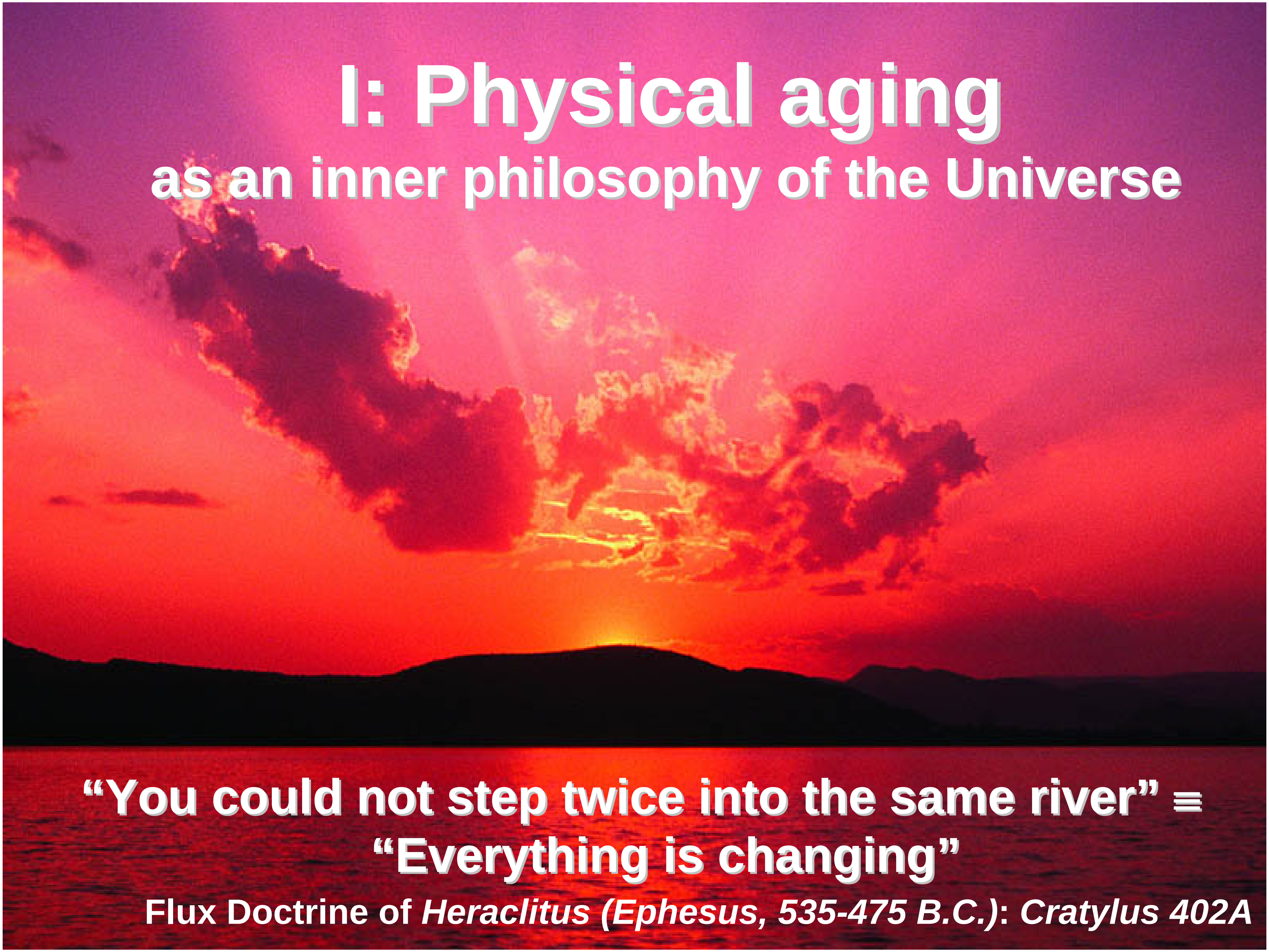
- **Introduction to the problem of Physical Aging:**
  - **- physical aging as an inner philosophy of the Universe;**
  - **- physical aging as a permanent feature of glass;**
  - **- “physical aging vs. reliability” controversy**
    as a motive force in the modern materials science of glass
- **On the methodology**
  to study Physical Aging in glass ***or***
  Conventional DSC vs. Temperature-Modulated DSC:
  What is the better?
- **Short-term vs. Long-term Physical Aging in chalcogenide glasses**
  (in terms of recent experimental results on As-Se glasses) ***or***
  How far should we go to understand
  an origin of Physical Aging in chalcogenide glasses?
- **A unified topological model**
  describing Physical Aging in chalcogenide glasses ***or***
  On the role of “straightening-shrinkage” nanostructural transformations
  in Physical Aging (exemplified by binary As-Se glass system)
- **On some practical aspects**
  in the field of Physical Aging in chalcogenide glasses ***or***
  “Acceleration-Stabilization” radiation-induced trends
  in Physical Aging of chalcogenide glasses
- **Instead of final remarks:**
  On the interconnection between Physical Aging
  in network glassy-like and biological systems

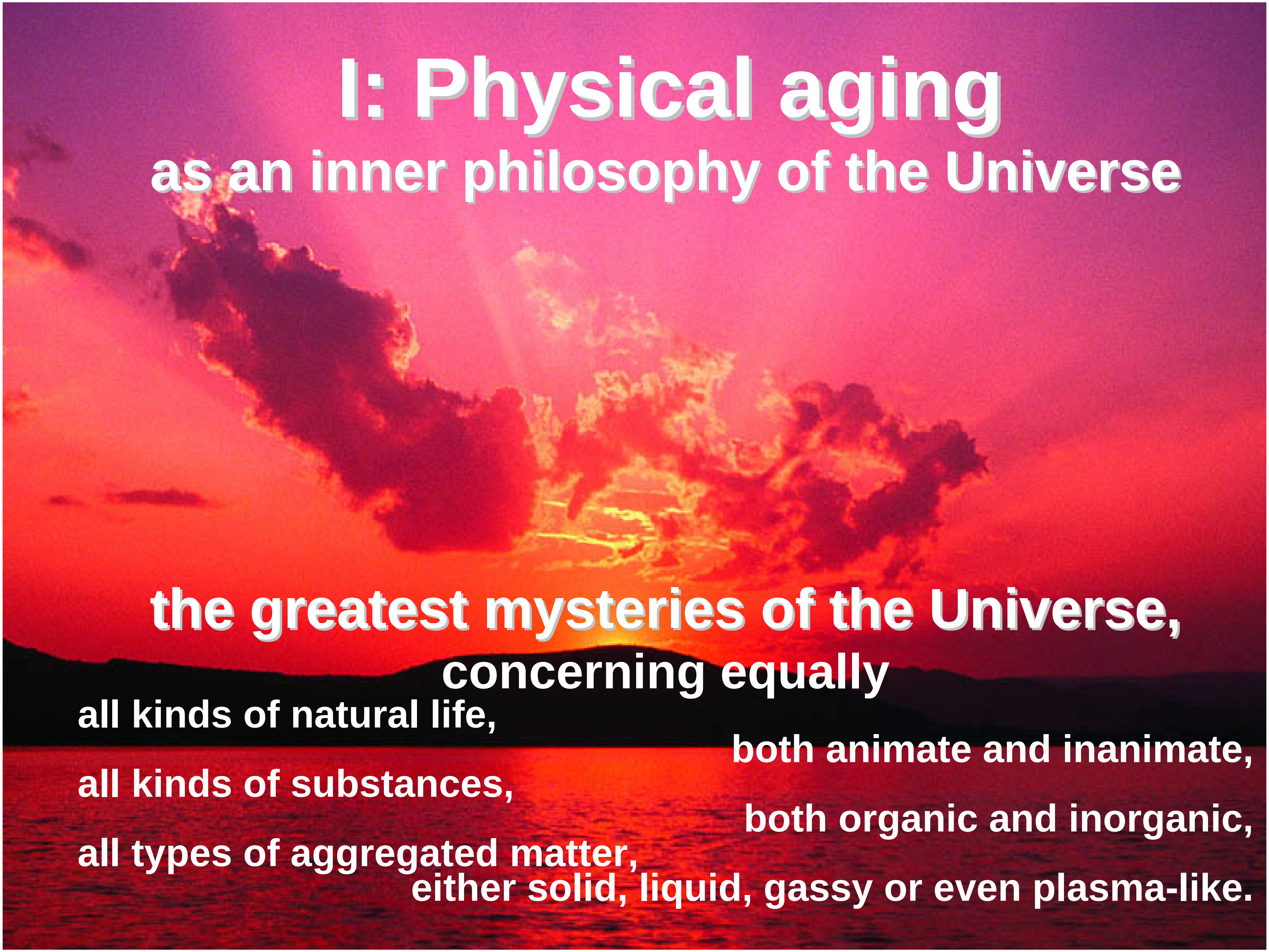
PHYSICAL AGING

in NANOSTRUCTURED TOPOLOGICALLY DISORDERED NETWORKs:

phenomenology,
mechanisms
and
prospects for new device application


I: Physical aging
as an inner philosophy of the Universe
affinity to physical aging
as a result to reach
the most energetically favorable state
of thermodynamic eqilibrium


I: Physical aging
as an inner philosophy of the Universe
“You could not step twice into the same river” ≡
“Everything is changing”
Flux Doctrine of *Heraclitus (Ephesus, 535-475 B.C.)*: *Cratylus 402A*


I: Physical aging
as an inner philosophy of the Universe
the greatest mysteries of the Universe,
concerning equally
all kinds of natural life,
both animate and inanimate,
all kinds of substances,
both organic and inorganic,
all types of aggregated matter,
either solid, liquid, gassy or even plasma-like.

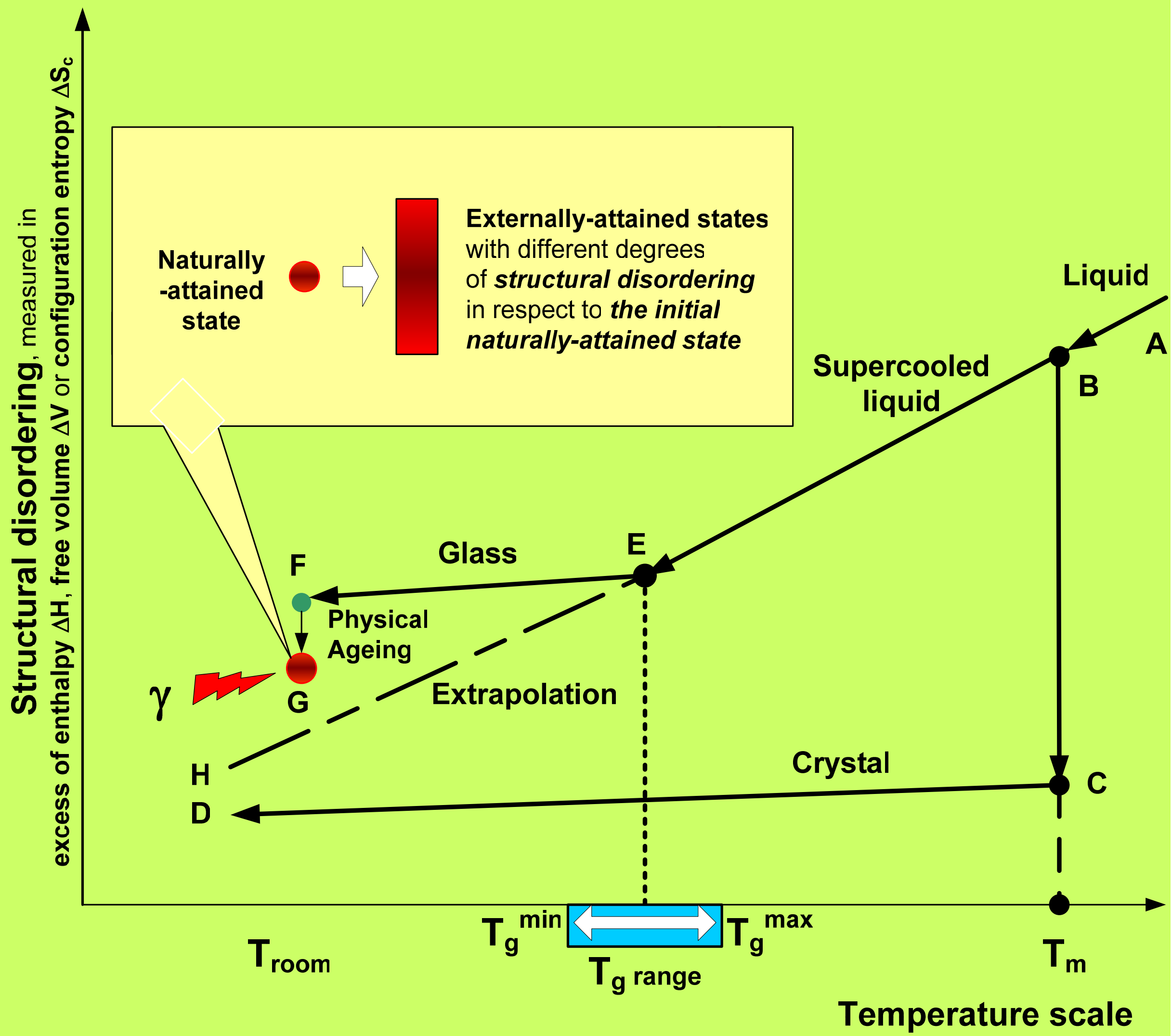
Physical aging

as a permanent feature of glass

Physical aging –
changes in physical-chemical properties of material (during natural storage) caused by its tending towards more thermodynamically equilibrium state.

Glass
is genetically always in metastable state owing to its origin.

Result of physical aging:
time-instability in exploitation characteristics of glass-based devices:
- optical and electrical memory systems;
- telecommunication and energy transfer;
- industrial sensorics;
- optical waveguide sensing and imaging.



Physical aging vs. Reliability

as a motive force in the modern materials science of glass

The problem:

the time uncertainty of physical aging itself

(the relaxation occurs with monotonically-decreased rate,
slowly tending towards saturation
during extraordinary long times)

The resolution:

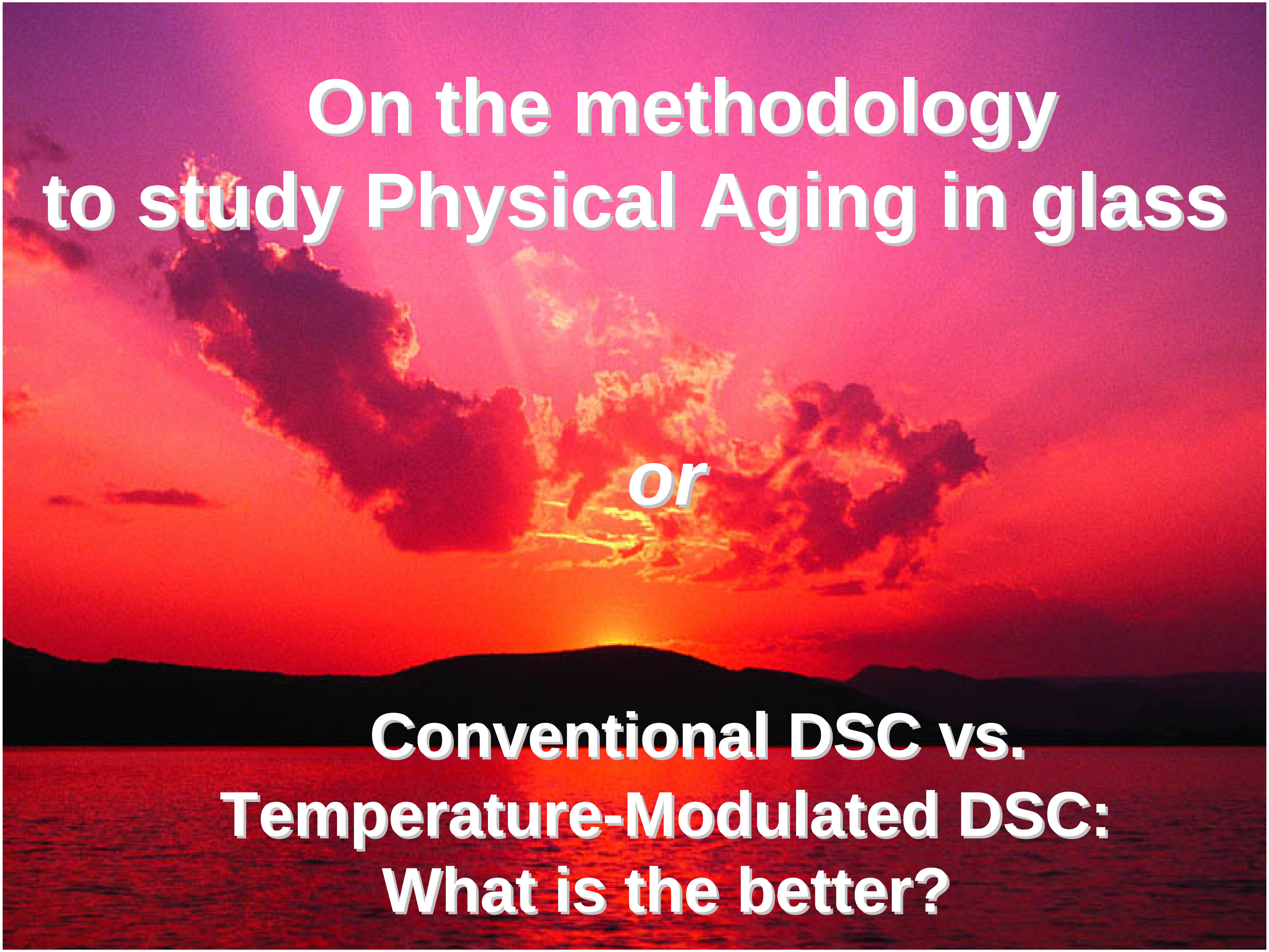
**the facilitation
of physical aging
in a time scale**

Physical aging

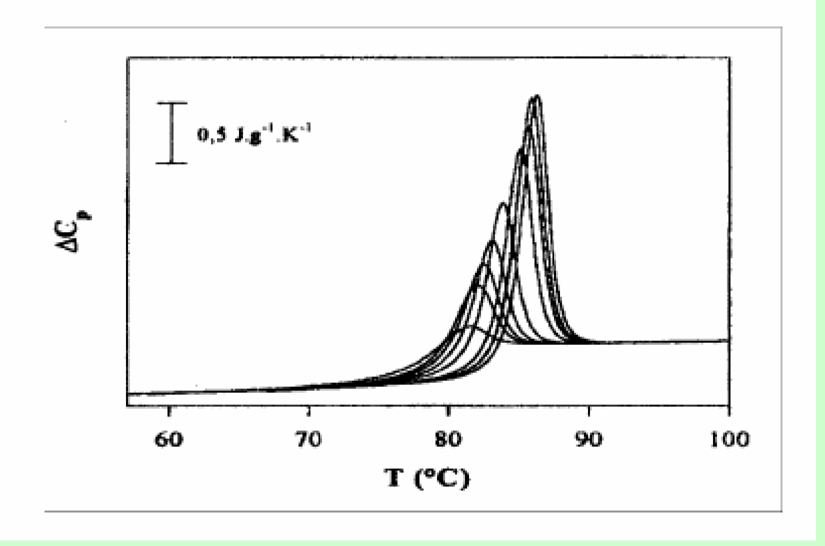
as overall tendency towards thermodynamic equilibrium

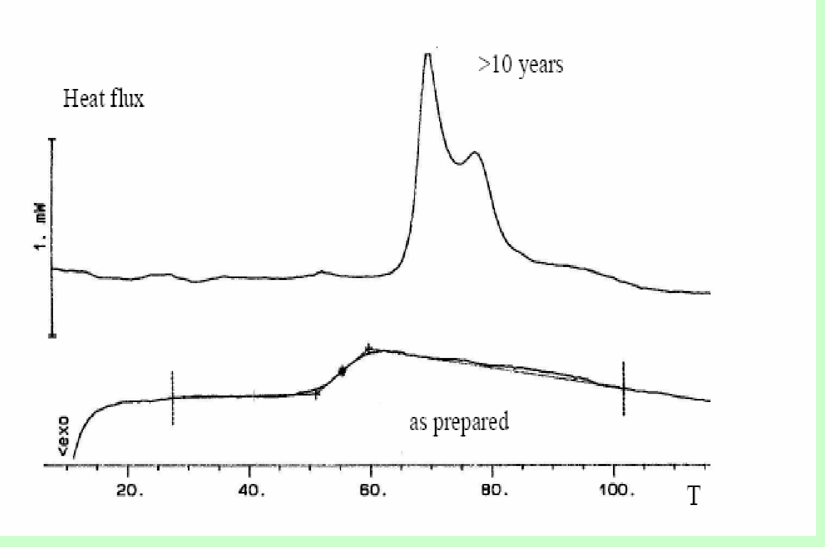
depends on **two factors:**

- **glass composition**
(types and content of chemical elements, glass-forming units and groups, etc.);
- **glass pre-history**
(cooling rate; additional thermal treatment near a glass transition;
duration, temperature, moisture and other environment conditions of time
exposure from as-prepared state; etc.).


On the methodology
to study Physical Aging in glass
or
Conventional DSC vs.
Temperature-Modulated DSC:
What is the better?

Physical aging in chalcogenide glasses:
methodological aspects





In terms of conventional DSC

(see: Saiter J.-M. Physical ageing in chalcogenide glasses. – J. Opto-electronics and Adv. Mat., 2001, v. 3, No 3, p. 685-694):

Typical DSC traces
(endothermic ΔC_p steps, C_p – thermodynamic specific heat) illustrating physical ageing in a chalcogenide glass kept at a constant temperature $T<T_g$ with different durations as increase in T_g value associated with an excess of enthalpy at T_g (the endothermic peak of relaxation is shifted toward higher temperatures and enthalpy increases).

Disadvantage of conventional DSC method:
To study physical aging, the separate experemental measurements are needed during whole period of sample storage, from "as-prepared" up to "very long aged" state.

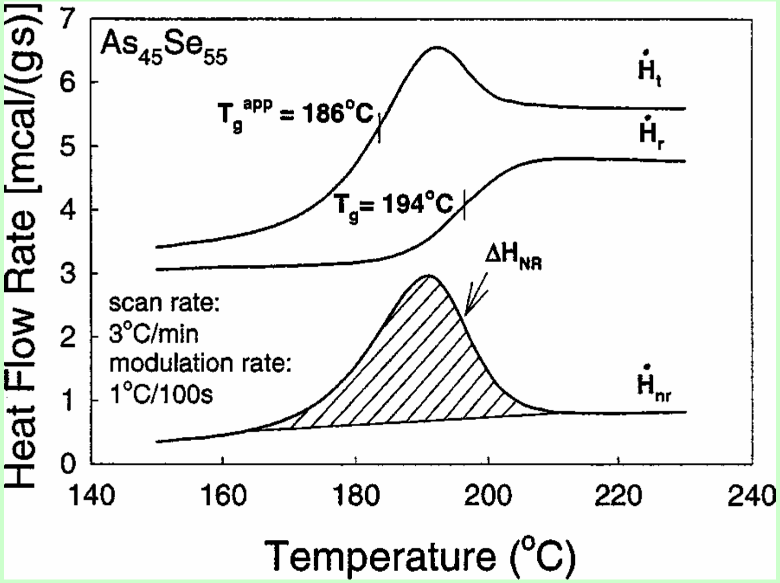
BUT

The most remarkable feature of the method:
as-prepared sample ≡ rejuvenated sample

Physical aging in terms of conventional DSC measurements:
difference in DSC traces for aged and rejuvenated glass samples

DSC traces obtained for Ge2Se98 glass aged more than 10 years at room temperature (the upper fig.) and for the same sample after rejuvenation (the lower fig.)
(the data are taken from: Saiter J.-M. Physical ageing in chalcogenide glasses. – J. Opto-electronics and Adv. Mat., 2001, v. 3, No 3, p. 685-694).

Physical aging in chalcogenide glasses:
methodological aspects



In terms of temperature modulated DSC (MDSC)

(see: Boolchand P., Georgiev D.G., Micolaut M. Nature of glass transition in chalcogenides. – J. Optoelectronics and Adv. Mat., 2002, v. 4, No 4, p. 823-836):

The basic idea:

A sinusoidal temperature $T_m\sin(\omega T)$ profile is superposed onto a fixed ramp dT/dt in programming a scan.

The consequence:

The total heat flow **dH_t/dt can be deconvoluted into the part, tracking T-modulations (ergodic or *reversing heat flow* dH_r/dt), and the remainder (non-ergodic or *non-reversing heat flow* dH_{nr}/dt).**

$$dH_t/dt = dH_r/dt + dH_{nr}/dt \qquad or$$

$$dH_t/dt = C_p dT/dt + dH_m/dt,$$

where C_p represents the thermodynamic specific heat.

Attempt to treat this approach as express-method of diagnostics for physical aging in a glass.

Physical aging in terms of MDSC measurements:

vanishing in non-reversing heat flow dH_{nr}/dT, measured in the early stages of physical aging

Disadvantage:

To permit a good heat transfer to the glass sample with a high reliable steady state heat flow, the modulation frequency ω should not exceed 0.03 Hz.

Correct resolution:

For more precise conclusion on physical aging in a glass,
the MDSC measurements should be repeated during relatively long time period.
Small changes in dH_{nr}/dt value
not detectable within conventional measuring accuracy during early stages of physical aging
can be accumulated multiply during very long time,
leading finally to significant changes in the final DSC traces for aged samples.

Short-term vs. Long-term Physical Aging in chalcogenide glasses

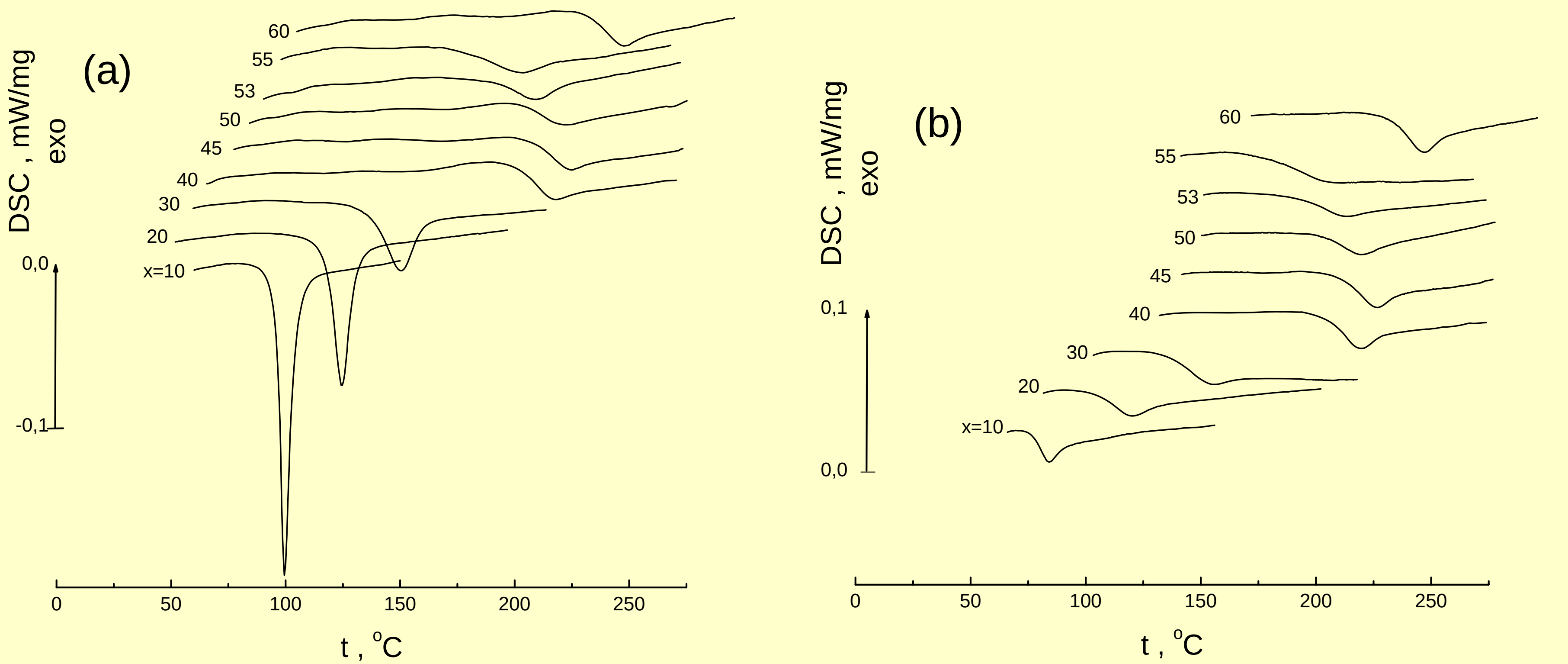
(in terms of recent experimental results on As-Se glasses)

or

How far should we go to understand an origin of Physical Aging in chalcogenide glasses?

Physical aging in chalcogenide glasses:

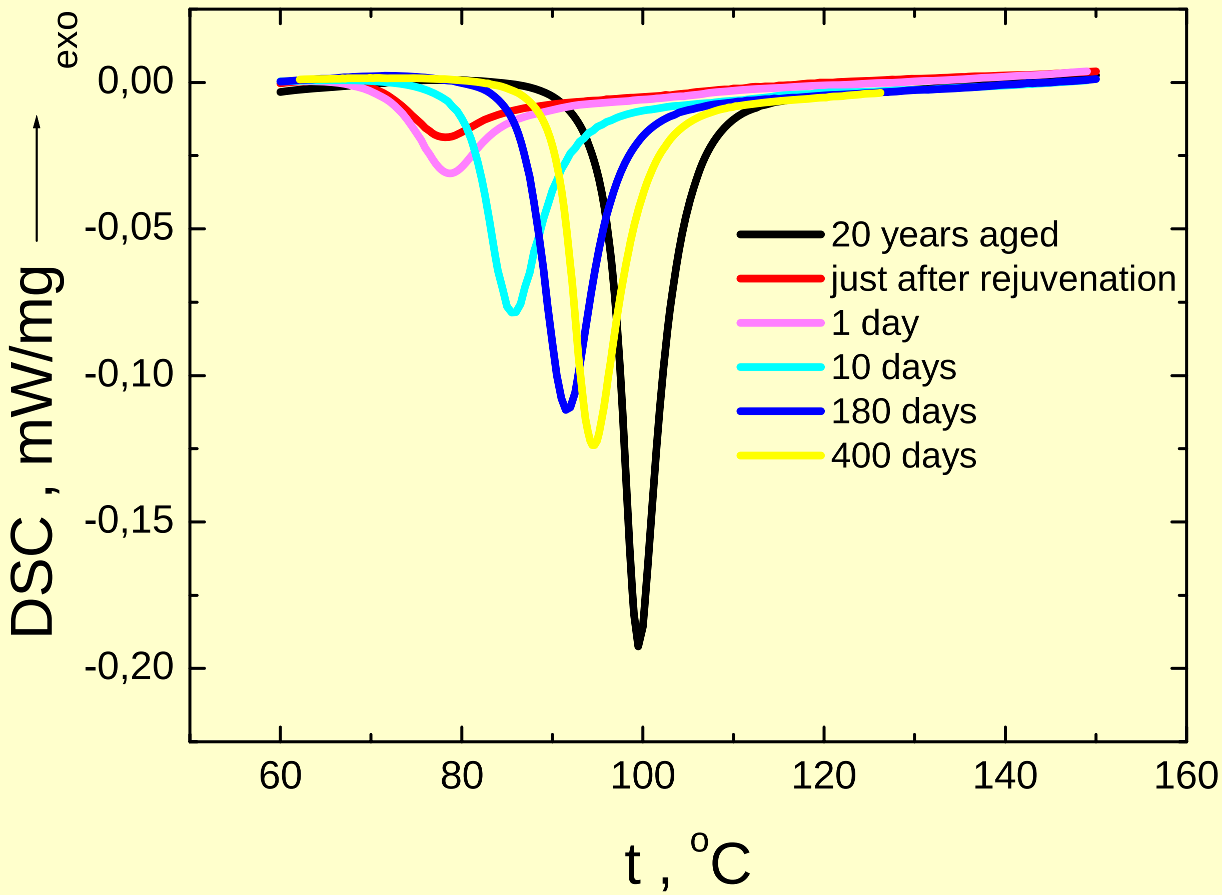
experimental results for g-As-Se



Typical DSC traces of g-As_xSe_{100-x}
subjected to 2-decade natural aging (a) *and* subsequent rejuvenation procedure (b)

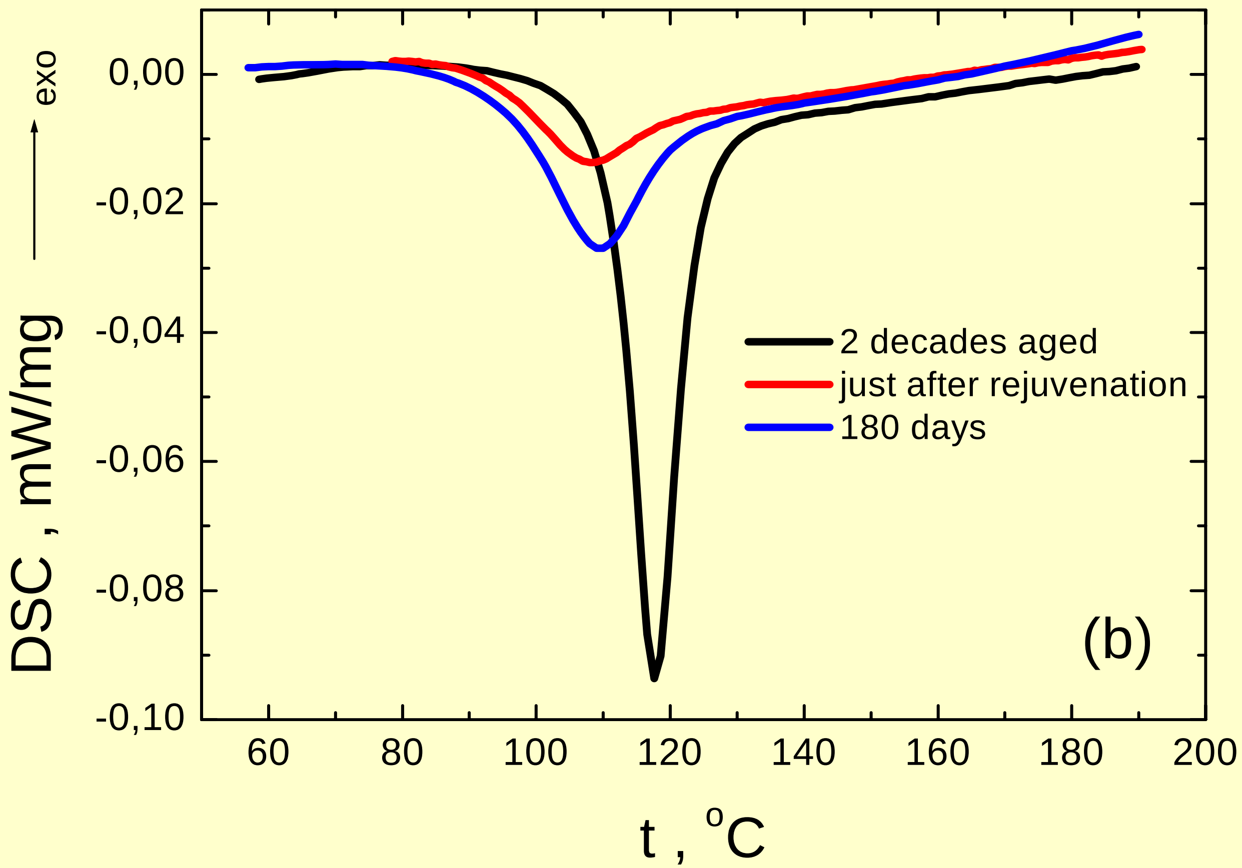
Physical aging in chalcogenide glasses:

experimental results for g-$As_{10}Se_{90}$



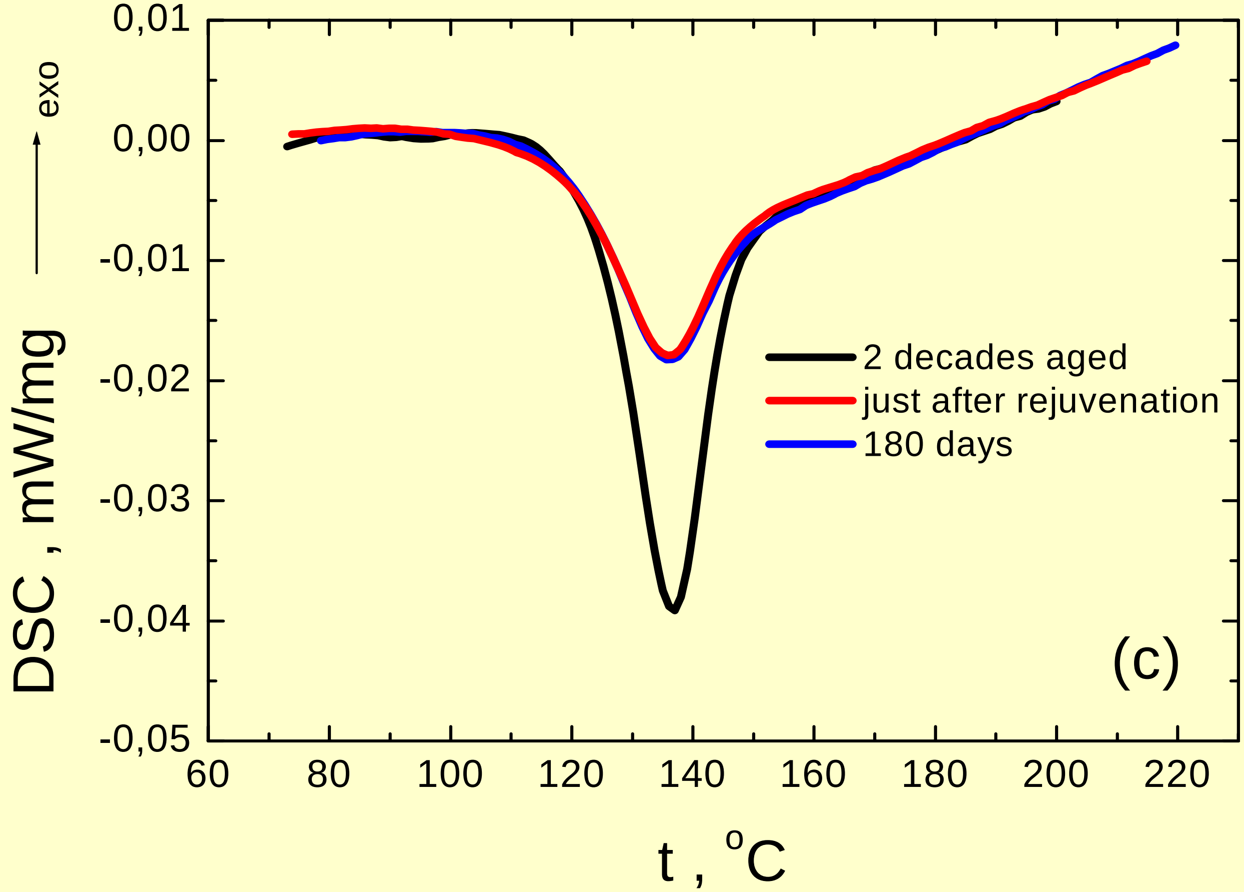
Evolution of DSC traces (q = 5 K/min)
showing kinetics of enthalpy lose in g-$As_{10}Se_{90}$

Physical aging in chalcogenide glasses:
experimental results for g-$As_{20}Se_{80}$



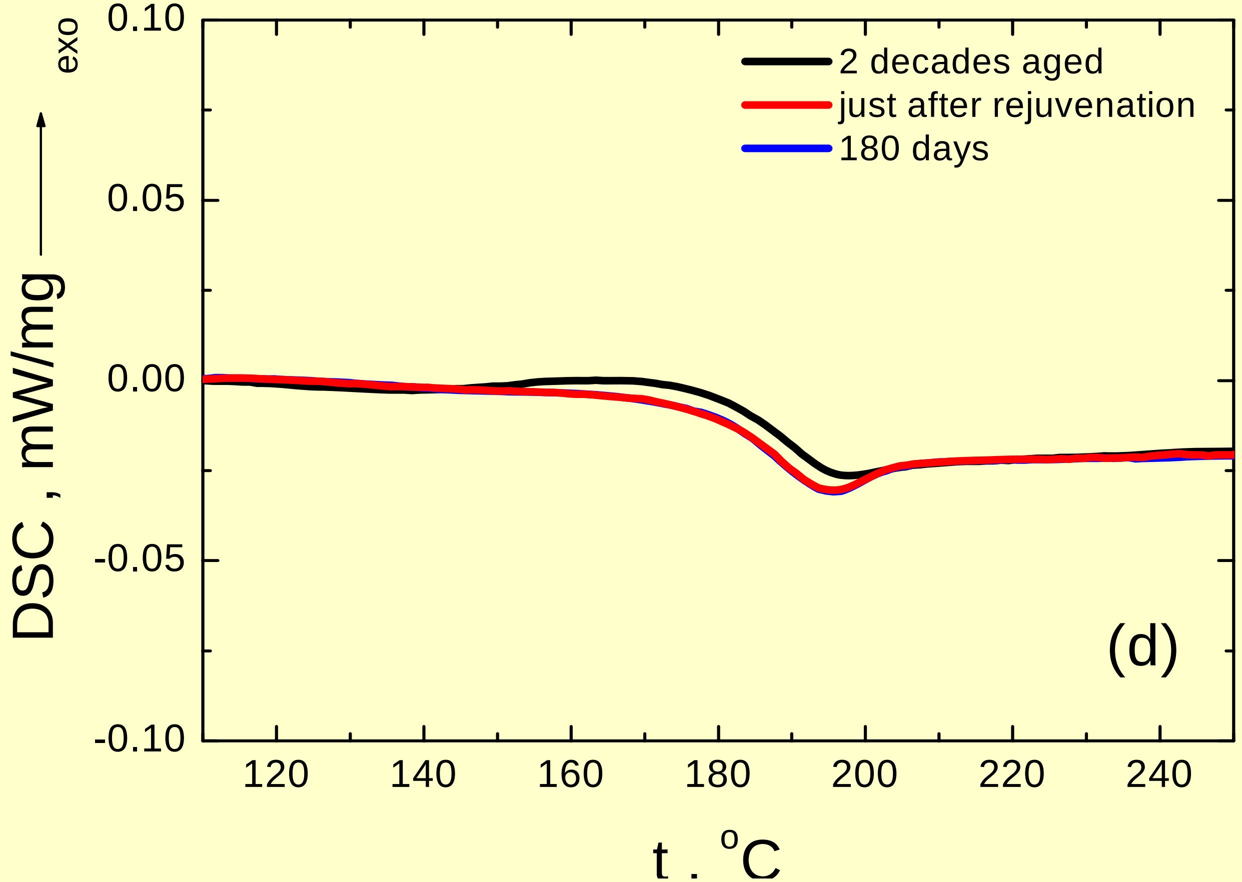
Evolution of DSC traces (q = 5 K/min)
showing kinetics of enthalpy lose in g-$As_{20}Se_{80}$

Physical aging in chalcogenide glasses:
experimental results for g-$As_{30}Se_{70}$



Evolution of DSC traces (q = 5 K/min)
showing kinetics of enthalpy lose in g-$As_{30}Se_{70}$

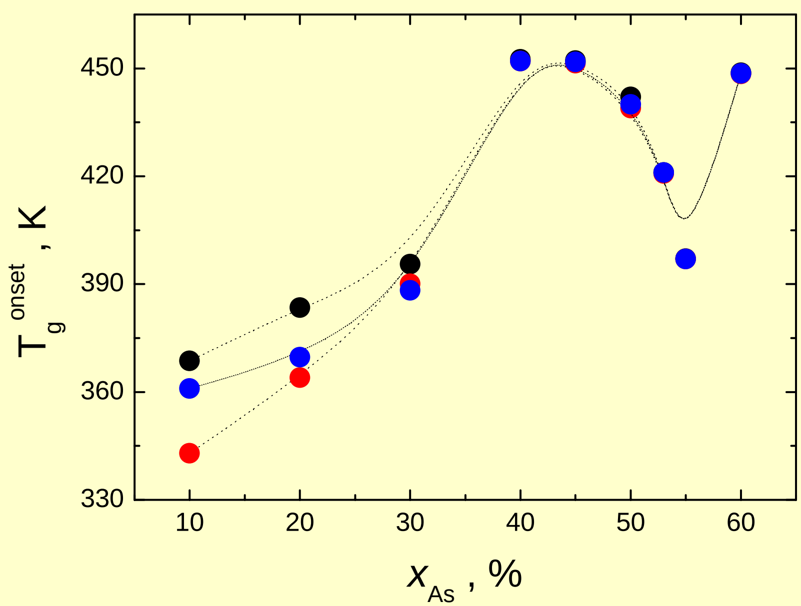
Physical aging in chalcogenide glasses:
experimental results for g-$As_{40}Se_{60}$

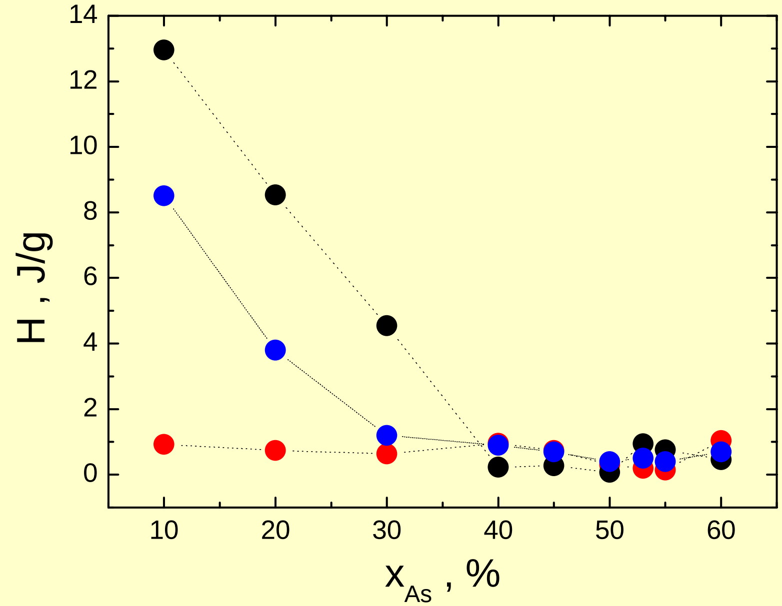


Evolution of DSC traces (q = 5 K/min)
showing kinetics of enthalpy lose in g-$As_{40}Se_{60}$

Physical aging in chalcogenide glasses:

experimental results for g-As-Se





Compositional dependences of T_g increase for 2-decade (black circles), 180-day aged (blue cycles) and rejuvenated (red cycles) g-As_xSe_{100-x}

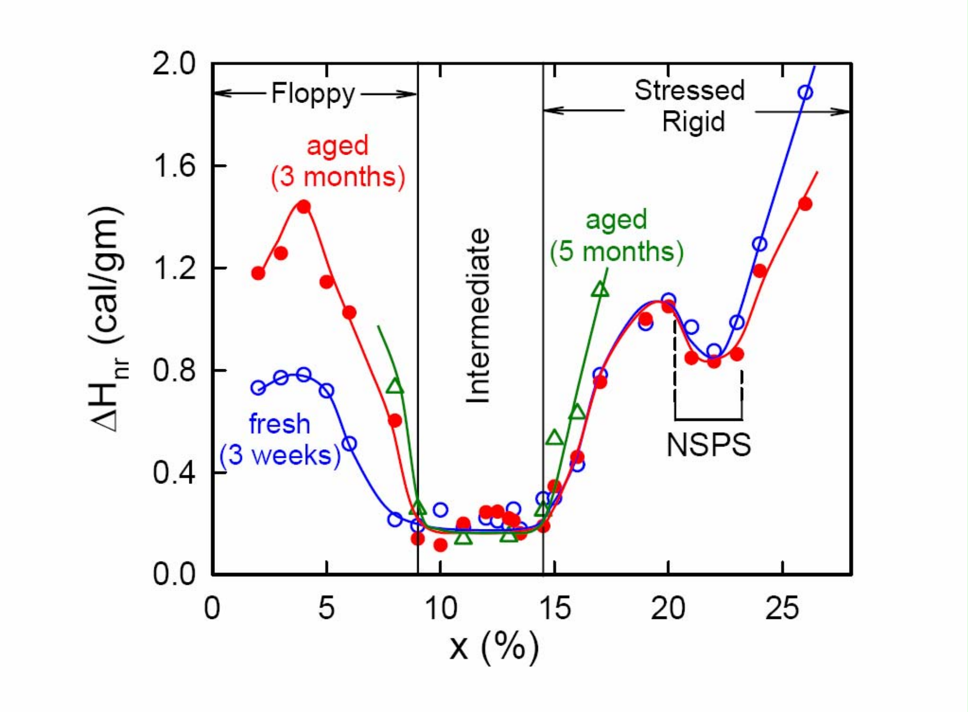
Compositional dependences of enthalpy losses ΔH for 2-decade (black circles), 180-day aged (blue cycles) and rejuvenated (red cycles) g-As_xSe_{100-x}

The CONTROVERSY:

short-term vs. long-term physical aging

Physical aging in g-As-Se:
short-term vs. long-term physical aging

Back to the METHODOLOGY:



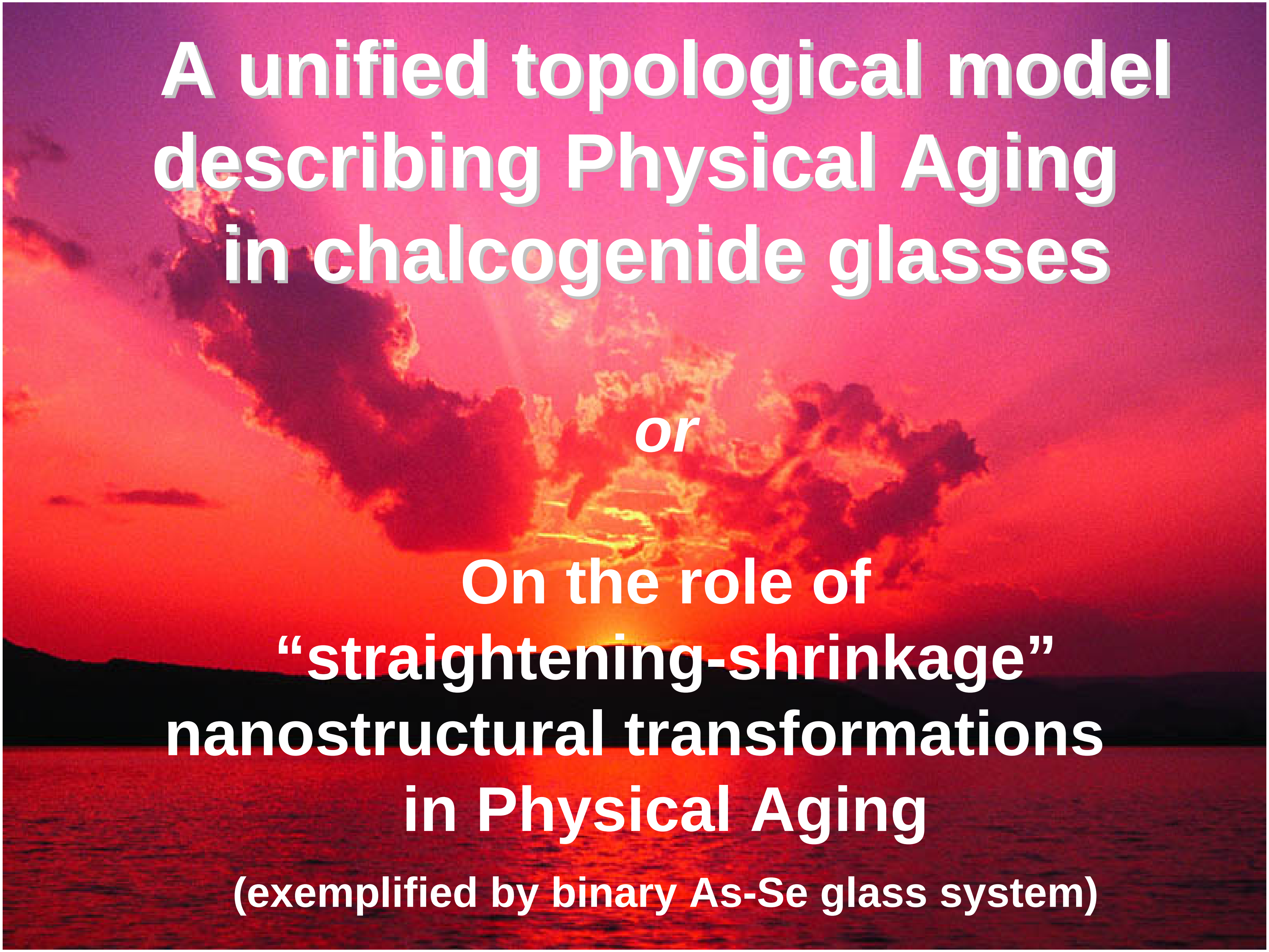
Can the effects of long-term physical aging be detected via MDSC measurements?

Shakravarty S., Georgiev D.G., Boolchand P., Micolaut M. Ageing, fragility and the reversibility window in bulk alloy glasses. – J. Phys.: Condens. Matter., 2005, v. 17, p. L1-L7.

The obvious controversy between *"sharpening/deepening"* and *"narrowing"* trends in the reversibility window (0.09<x<0.145) for g-$Ge_xP_xSe_{1-2x}$ with ageing duration at 300 K.

Resolution:

For more precise conclusion on physical aging in a glass, the MDSC measurements should be repeated few times during relatively long aging period.

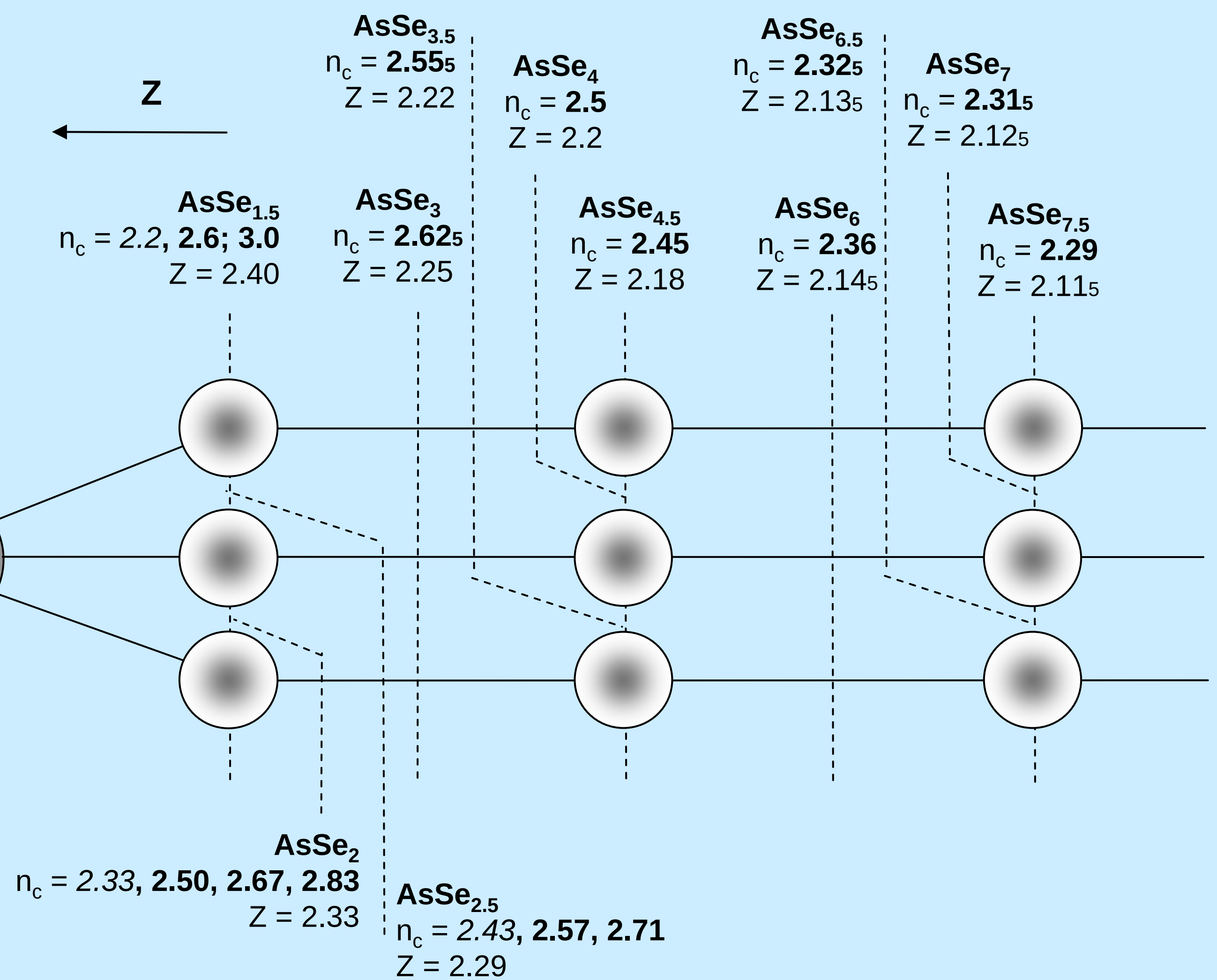

A unified topological model describing Physical Aging in chalcogenide glasses
or
On the role of "straightening-shrinkage" nanostructural transformations in Physical Aging
(exemplified by binary As-Se glass system)

Structure of g-As-Se in the terms of "CHAIN-CROSSING MODEL"

<u>Main postulate:</u> As atoms are homogeneously distributed within glass-forming network
(Se-based chains are cross-linking $AsSe_3$ pyramids,
the number of Se atoms between two pyramids depending on the glass composition)

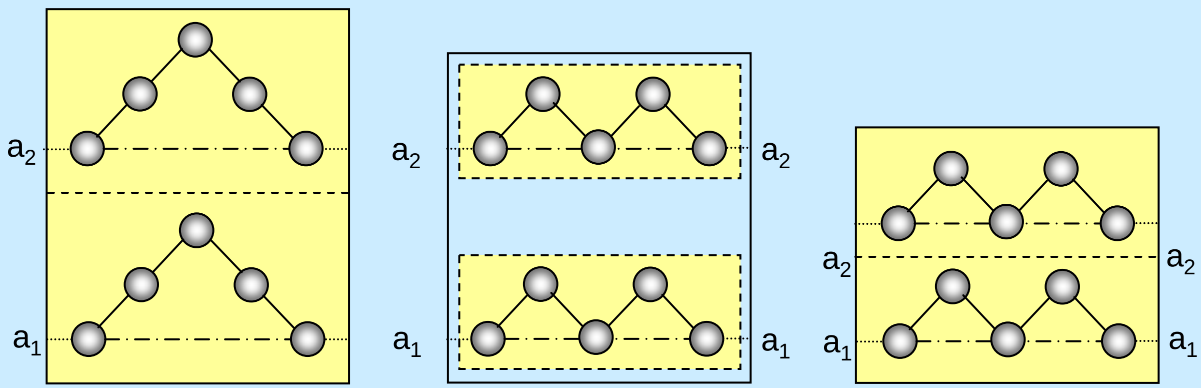
No	Main topological elements uniformly-distributed within glass-forming network		Compo-sition, Z	Structure characterization	
	Full signature	Short signature		Type of glass-forming structural units	Topological type
1	**>As–Se–As<**	**>As–Se$_1$–As< ($AsSe_3$)–As=**	**$AsSe_{1.5}$ 2.40**	directly-linked corner- or edge-sharing pyramids (>As-Se-As< or -As<Se$_2$>As- bridges)	2D-type layered structure (D=2)
2	**>As–Se–Se–As<**	**>As–Se$_2$–As< ($AsSe_3$)–($AsSe_3$)**	**$AsSe_3$ 2.25**	-Se-Se-linked corner-sharing pyramids (>As-Se-Se-As< bridges)	Pyramids + (Se-Se) bonds
3	**>As–Se–Se–Se–As<**	**>As–Se$_3$–As< ($AsSe_3$)–(Se)$_1$–($AsSe_3$)**	**$AsSe_{4.5}$ 2.18**	"quasi-chains" + pyramids	1D-type chain-like structure (1≤D<2)
4	>As–Se–Se–Se–Se–As<	>As–Se$_4$–As< ($AsSe_3$)–(Se)$_2$–($AsSe_3$)	**$AsSe_6$ 2.145**		
5	**>As–Se–Se–Se–Se–Se–As<**	**>As–Se$_5$–As< ($AsSe_3$)–(Se)$_3$–($AsSe_3$)**	**$AsSe_{7.5}$ 2.115**	chains + pyramids	
6	>As–Se–Se–Se–Se–Se–Se–As<	>As–Se$_6$–As< ($AsSe_3$)–(Se)$_4$–($AsSe_3$)	**$AsSe_9$ 2.10**		
7	>As–Se–Se–Se–Se–Se–Se–Se–As<	>As–Se$_7$–As< ($AsSe_3$)–(Se)$_5$–($AsSe_3$)	**$AsSe_{10.5}$ 2.085**		
8	**>As–Se–Se–Se–Se–Se–Se–Se–Se–As<**	**>As–Se$_8$–As< ($AsSe_3$)–(Se)$_6$–($AsSe_3$)**	**$AsSe_{12}$ 2.075**	"quasi-rings" + chains + pyramids	1D-type ring-chain-like structure (0≤D≤1)
9	>As–Se–Se–Se–Se–Se–Se–Se–Se–Se–As<	>As–Se$_9$–As< ($AsSe_3$)–(Se)$_7$–($AsSe_3$)	**$AsSe_{13.5}$ 2.07**		
10	**>As–Se–Se–Se–Se–Se–Se–Se–Se–Se–Se–As<**	**>As–Se$_{10}$–As< ($AsSe_3$)–(Se)$_8$–($AsSe_3$)**	**$AsSe_{15}$ 2.065**	rings + chains + pyramids	
11	>As–Se–Se–Se–Se–Se–Se–Se–Se–Se–Se–Se–As<	>As–Se$_{11}$–As< ($AsSe_3$)–(Se)$_9$–($AsSe_3$)	**$AsSe_{16.5}$ 2.055**		

"Chain-crossing model" for g-As-Se
supported by constraint-counting algorithm



Physical aging in g-As-Se: the model

Schematic illustration showing subsequent stages of "straightening" and "shrinkage" effects in Se-enriched covalent-bonded glass backbone caused by short-term physical ageing



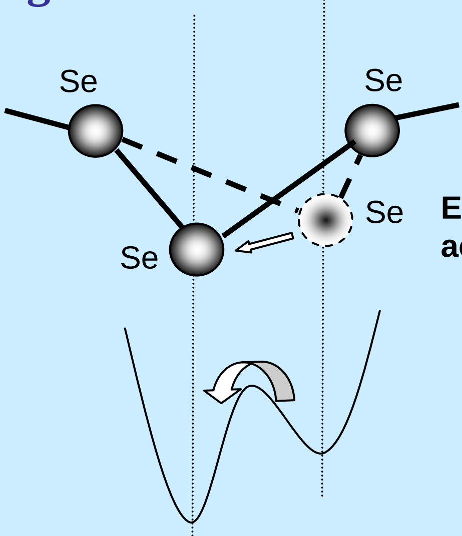
Initial state
(before ageing)

Straightening effect

Shrinkage effect

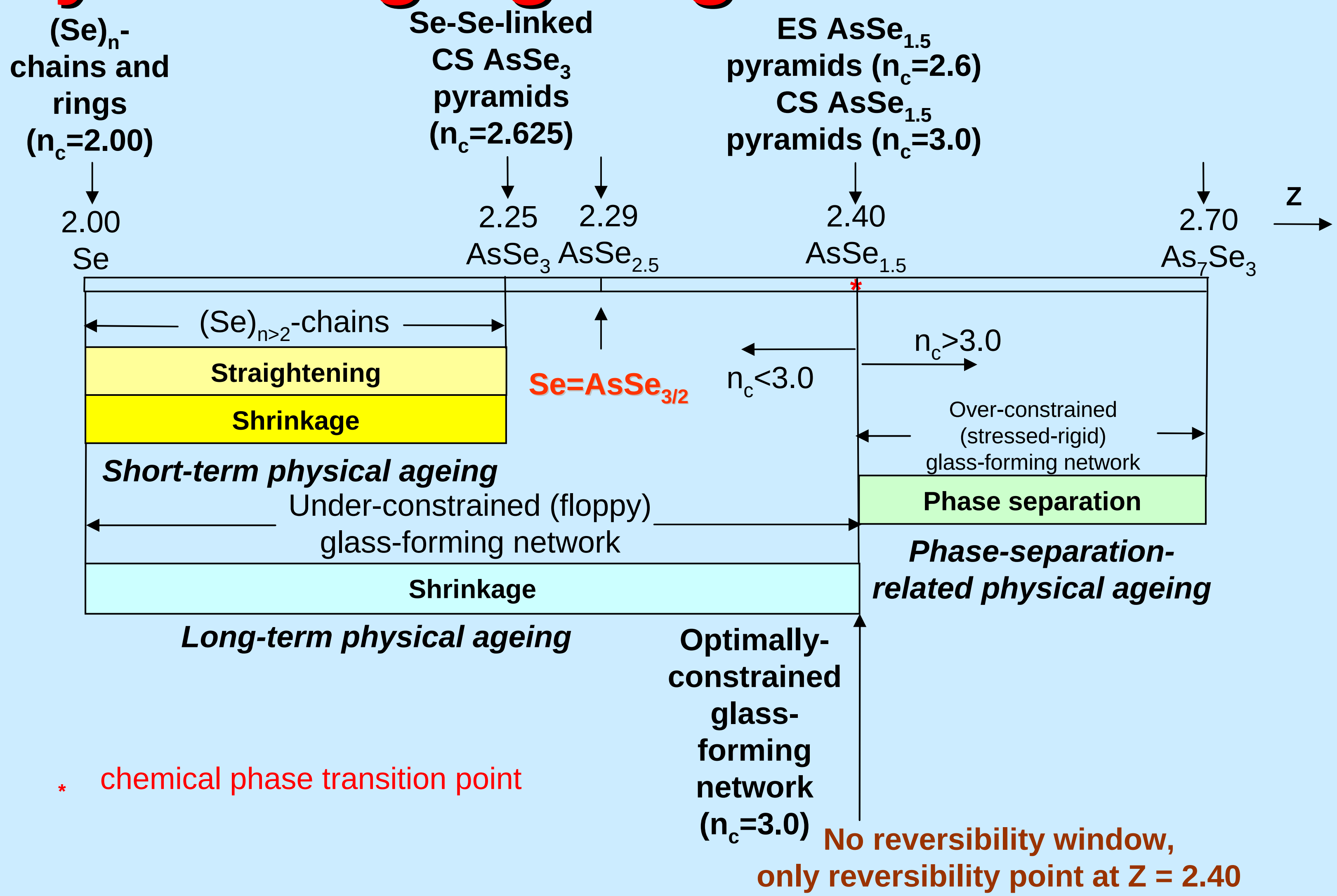
a-a – axis line of chain-crossing structural units

Straightening bent deformations of chains occur via boundary displacements of bridge chalcogen atoms within double-well potential (DWP) as elementary relaxation acts



Elementary relaxation act ⇨ **Straightening of bent-deformed Se chains** ⇨ **Decrease in mean square deviation of Se atoms from basic line within one chain-crossing s.u.**

Physical aging in g-As-Se: the model



Disproportionality reaction for -(Se_2)-point:

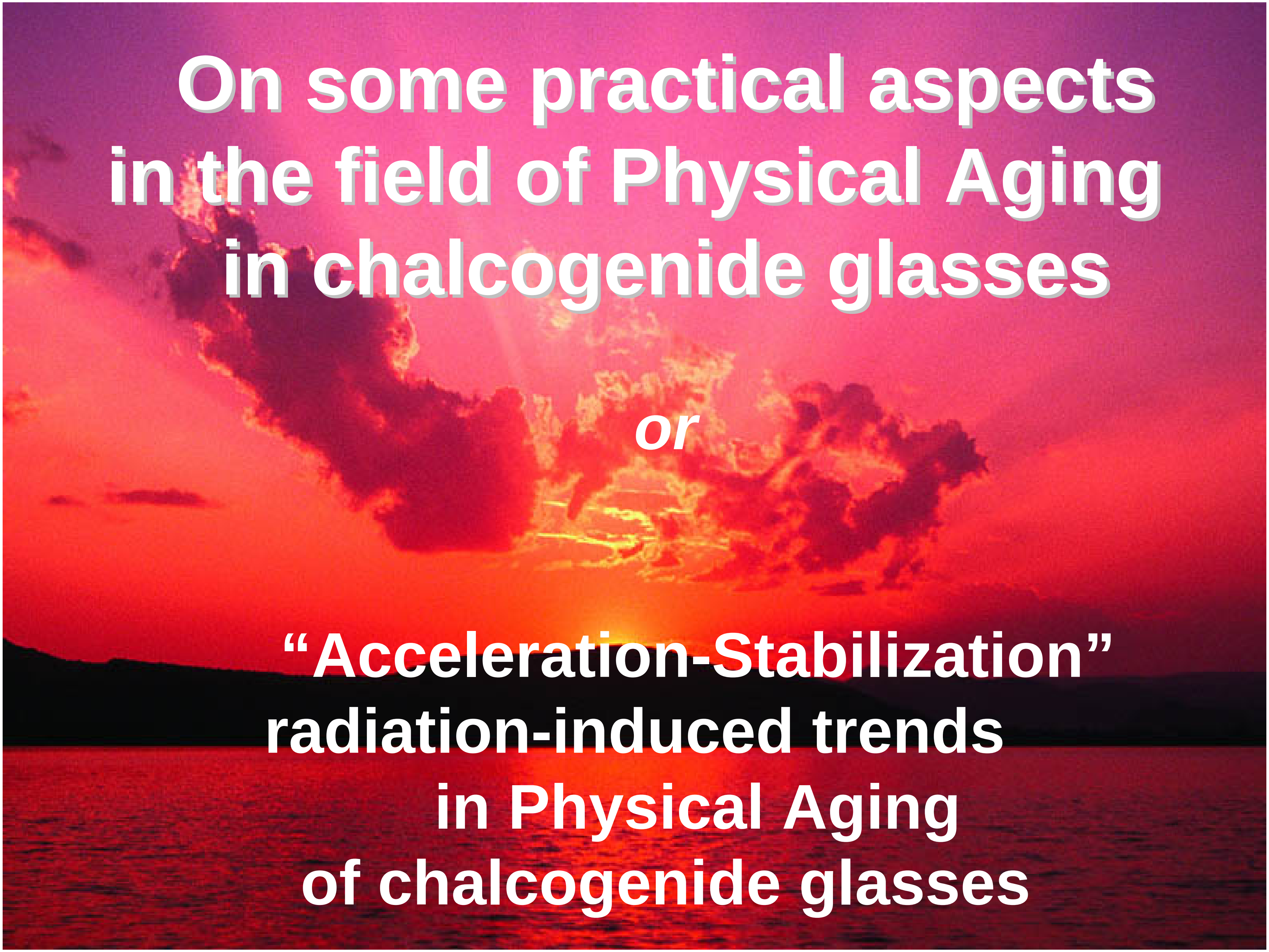
As_xSe_{1-x} = xAsSe3

1-x = 3x; x = 0.25; **Z = 2.25**

Disproportionality reaction for optimally-constrained glasses (n_c = 3.0):

As_xSe_{1-x} = xAsSe1.5

1-x = 1.5x; 2.5x = 1; x = 0.4; **Z = 2.4**


On some practical aspects
in the field of Physical Aging
in chalcogenide glasses
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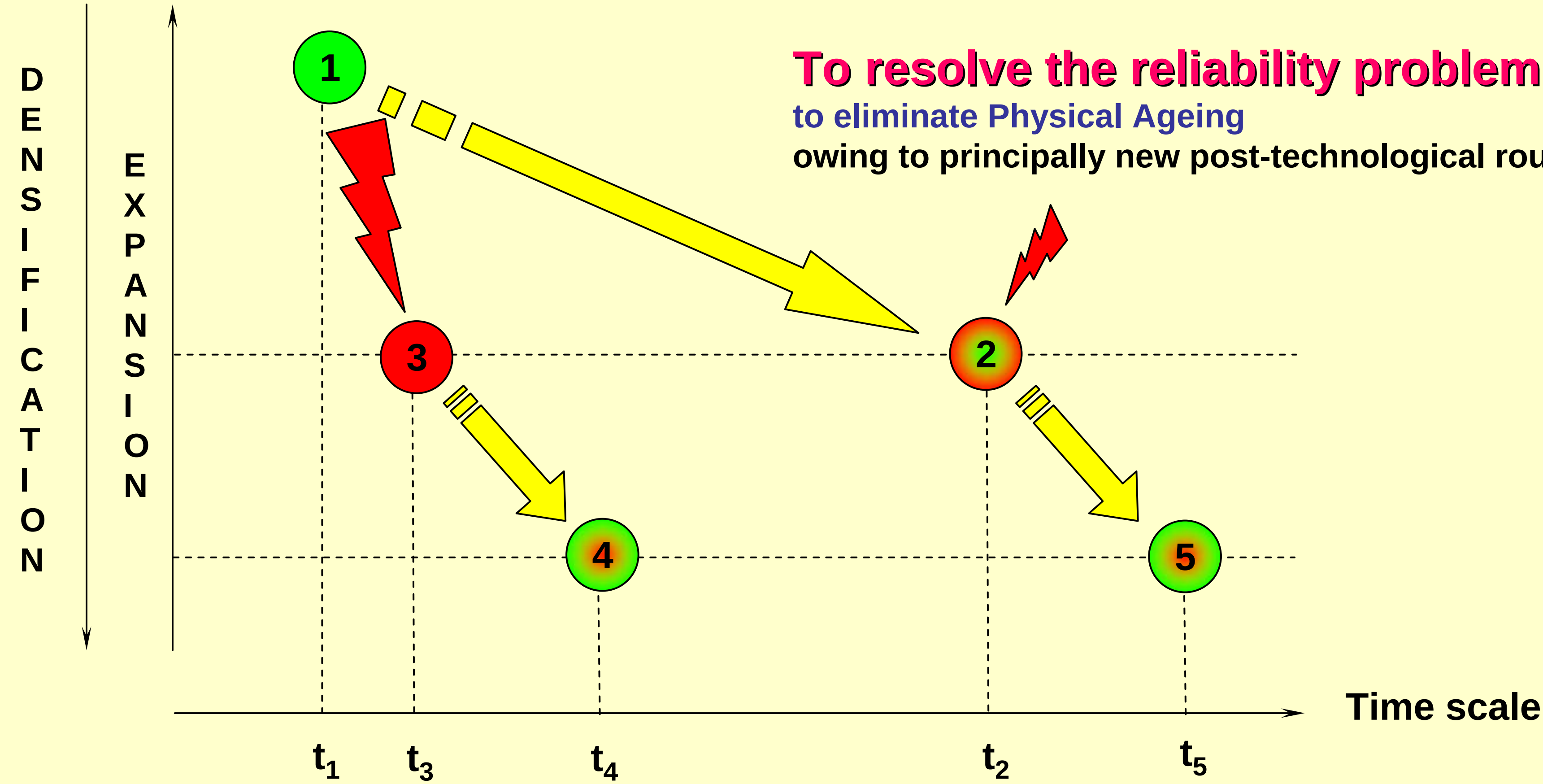
"Acceleration-Stabilization"
radiation-induced trends
in Physical Aging
of chalcogenide glasses

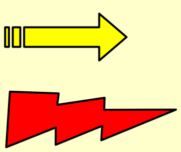
Physical aging vs. Reliability

as a motive force in the modern materials science of glass



To resolve the reliability problem:
to eliminate Physical Ageing
owing to principally new post-technological route

Physical Ageing:



Natural

Externally-Induced

1 – as-prepared glass (via conventional melt-quenching route)
2 – naturally-aged as-prepared glass (1-2 – long-term physical aging)
3 – externally-aged as-prepared glass
(1-3 – pure externally-induced physical aging)
4 – naturally-aged externally-modified glass
(3-4 – additional input owing to external influence in 1 point)
5 – naturally-aged externally-modified glass
(2-5 – additional input owing to external influence in 2 point)

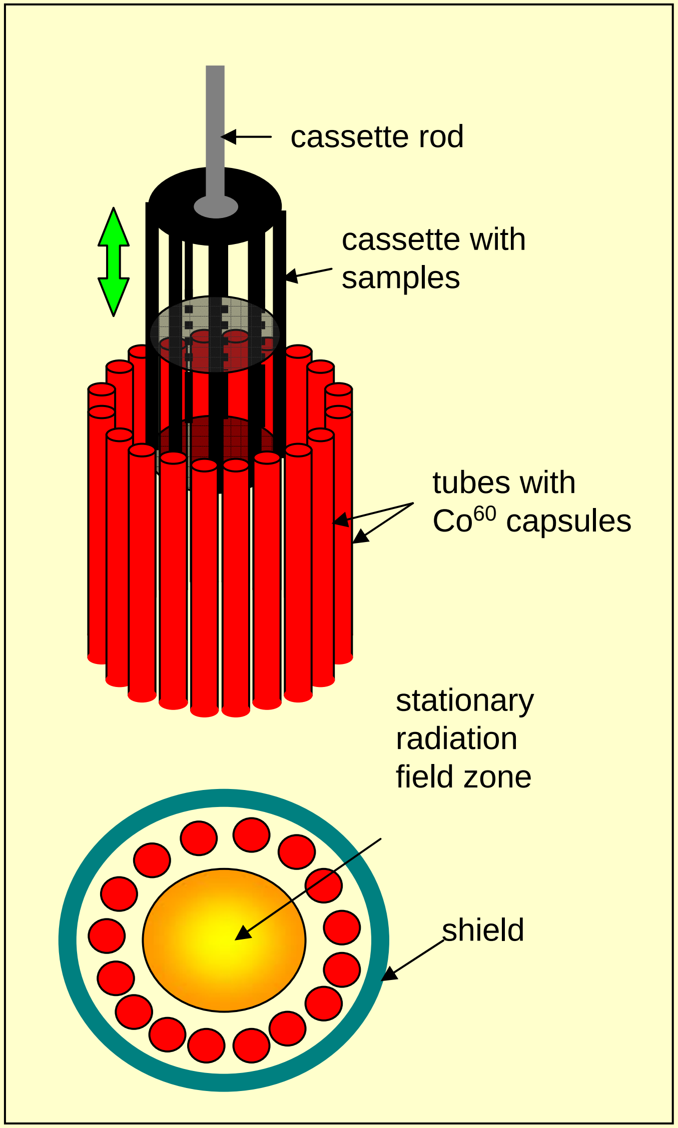
Irradiation treatment

Numerical parameters and geometry of γ-irradiation:

Radiation treatment is usually performed in the normal conditions of **stationary radiation field**, created in a closed cylindrical cavity by a number of concentrically established ***^{60}Co (E=1.25 MeV)*** radioisotope capsules.

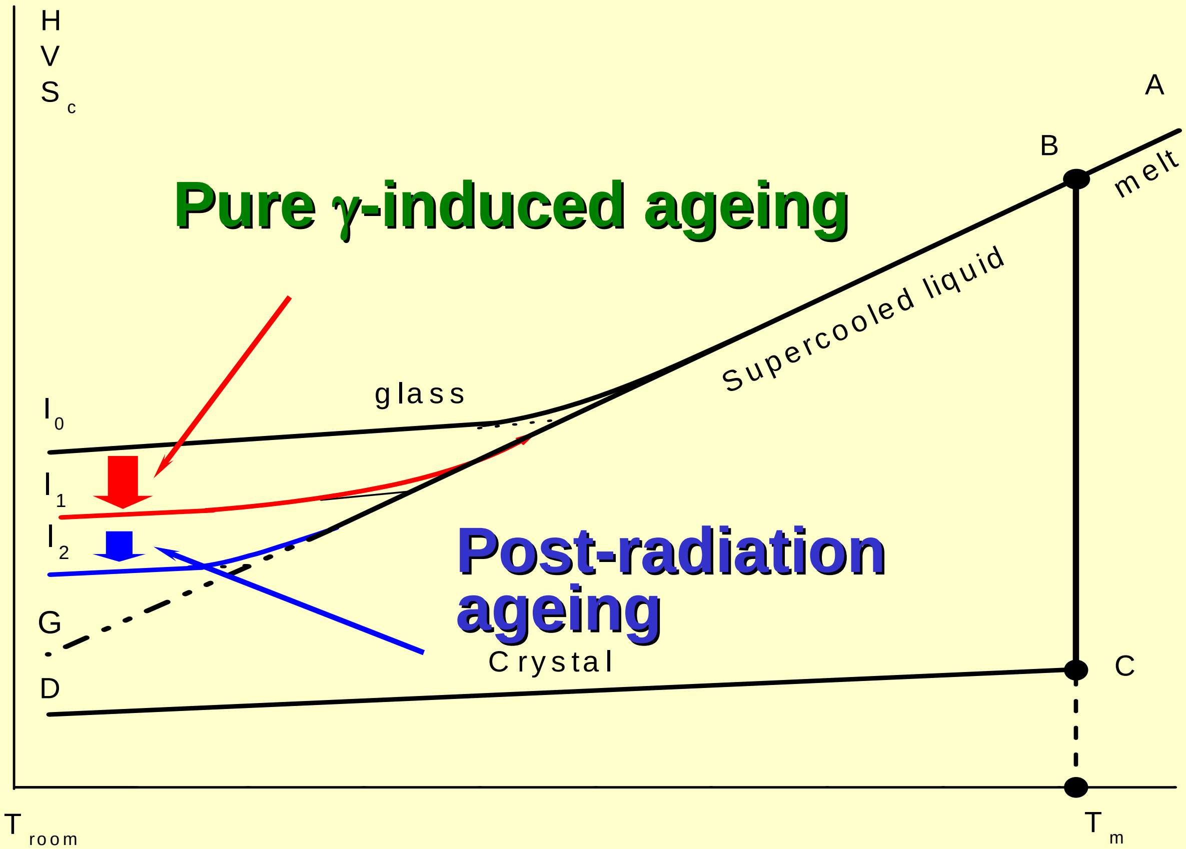
The accumulated doses of ***Φ=0.1-10.0 MGy*** were chosen with account of the previous results of I.A. Domoryad (1960-s).

The absorbed dose power P was chosen ***from a few up to 25 Gy/s***. This P value determined ***the maximum temperature of accompanying thermal heating*** in irradiating chamber. This temperature did not exceed ***310-320 K*** during prolonged γ-irradiation (more than 10 days), provided dose power ***P<5 Gy/s***, but it reached even ***380-390 K*** at the dose power of ***~25 Gy/s***.



Radiation-induced effects in physical aging

Three types of Physical Aging Effects in respect to γ-irradiation treatment:



Effect No 1:
Pure Natural Physical Aging –
Physical Aging of glass under natural storage (in normal conditions)

Effect No 2:
Pure γ-induced Physical Aging –
Physical Aging of glass under γ-irradiation (in stationary radiation field conditions)

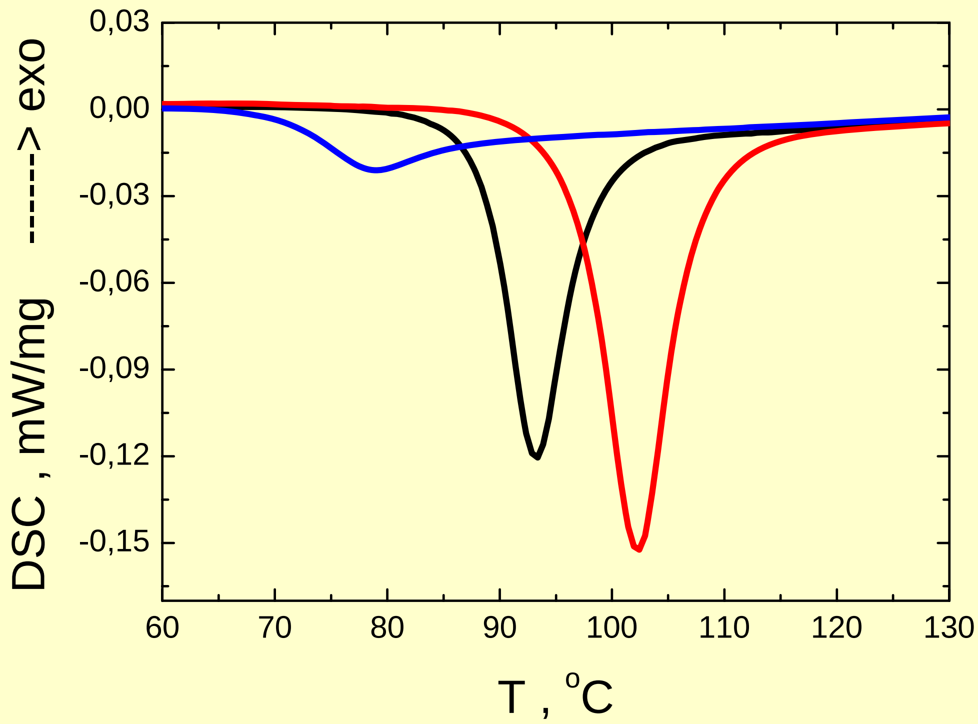
Effect No 3:
Post-irradiation Natural Physical Aging –
Physical Aging of just-irradiated glass under natural storage (in normal conditions)

Effect No 2 – Effect No 1 ≡ Transition $I_0 \Rightarrow I_1$ *or* "acceleration" trend in physical aging

Effect No 3 – Effect No 2 ≡ Transition $I_1 \Rightarrow I_2$ *or* "stabilization" trend in physical aging

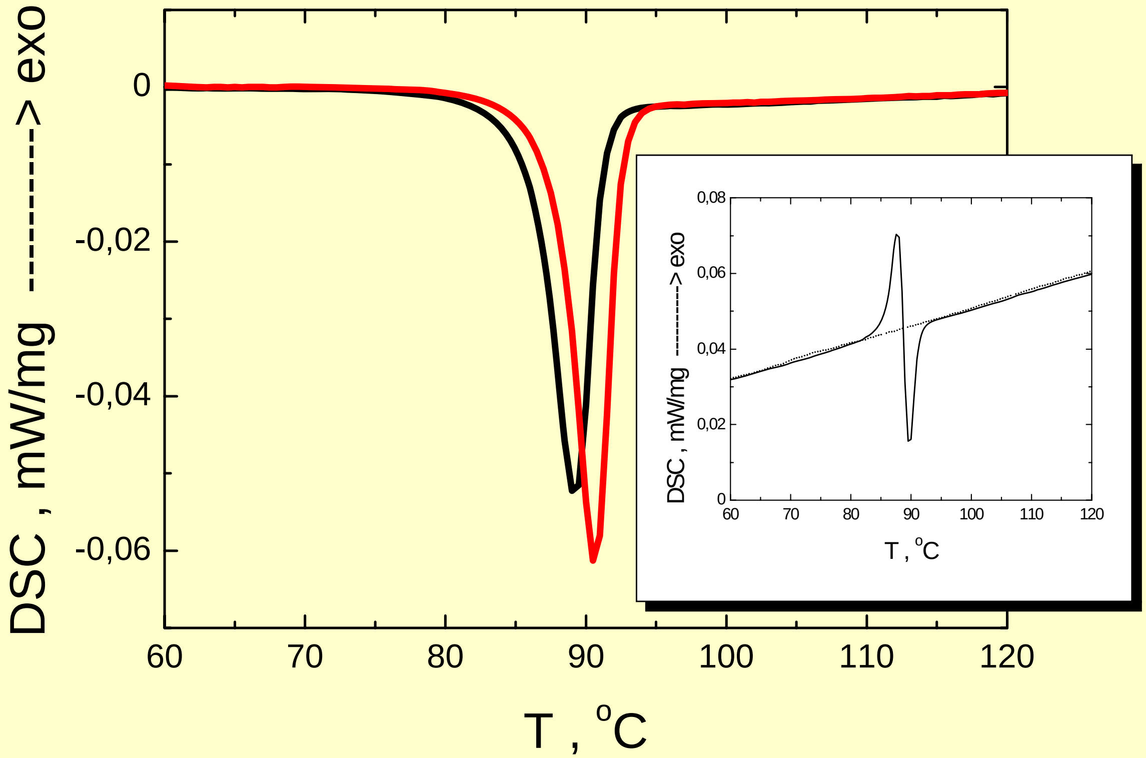
Effect No 3 – Effect No 1 ≡ Transition $I_0 \Rightarrow I_1 \Rightarrow I_2$ *or* overall modification trend in physical aging

Radiation-induced effects in physical aging:
"acceleration" trend



DSC traces (q = 5 K/min) of g-$As_{10}Se_{90}$:
rejuvenated (blue),
6-months aged without γ-irradiation (black) *and*
4-months aged followed by 2-months γ-irradiation (red)

Radiation-induced effects in physical aging:
"stabilization" trend



DSC traces (q = 1 K/min) of g-$As_{10}Se_{90}$ samples:
20-years aged (black) *and*
20-years aged followed by additional γ-irradiation and 1-year natural aging (red)

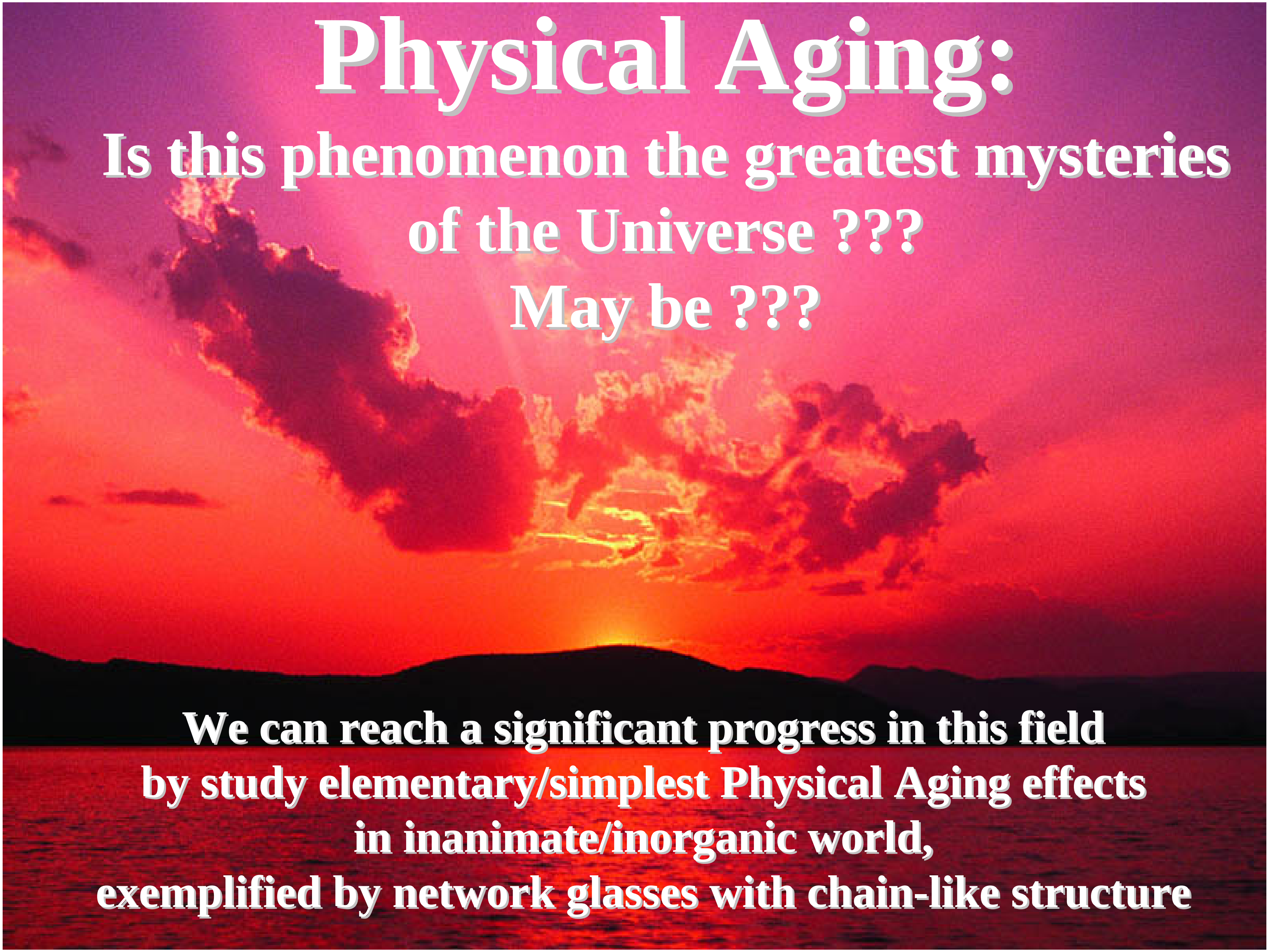
Instead of final remarks:

Physical Aging in network glasses as key step to understand the nature of aging in living systems

The reason:

*1) **the chain-like structural fragments***
are supposed to be
the common feature of both
organic *and*
inorganic nanonetworks;

2) ***the discreteness of kinetic processes***
is proper for both
network glasses
(the kinetics is determined only by a glass structure) *and*
biological populations
(despite obvious complexness, the kinetics is determined by genetic factors, having structural nature too).


Physical Aging:
Is this phenomenon the greatest mysteries
of the Universe ???
May be ???
We can reach a significant progress in this field
by study elementary/simplest Physical Aging effects
in inanimate/inorganic world,
exemplified by network glasses with chain-like structure


Thank You
for high attention