

## Twofold Facet of Kinetics of Glass Aging

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 (Received 20 March 2024; accepted 24 June 2024; published 25 July 2024)

We employ fast scanning calorimetry to monitor the isothermal aging kinetics in glassy polymers, complemented with measurements on other glasses. Apart from following the time evolution of the glass enthalpic state, we monitor the aging kinetics of the devitrification width on heating,  $\Delta T_{\text{dev}}$ . We find that significantly below the glass transition temperature,  $T_g$ , the glass enthalpy attains equilibrium earlier than  $\Delta T_{\text{dev}}$ , which evolves at long aging times toward enhanced heterogeneity. Hence, our results indicate that the description of time dependent evolution in glassy materials requires information beyond the mere description of its enthalpic state.

DOI: 10.1103/PhysRevLett.133.048201

Glasses are solid materials ubiquitous in nature consisting of frozen-in disorder [1,2]. Routes to glass formation are manifold. That of cooling a liquid, previously supercooled below its melting temperature,  $T_M$ , through its glass transition, a phenomenon addressed as vitrification, is the most common [1]. The so-obtained glasses below the glass transition temperature,  $T_g$ , are in nonequilibrium with respect to the supercooled liquid and, therefore, their thermodynamic state exhibits time dependent evolution toward equilibrium, a phenomenon addressed as structural recovery [3] or physical aging [4,5].

A system in the gas, liquid, or solid state can be uniquely defined according to its free energy and its associated enthalpy, entropy, or specific volume. A similar approach has been historically followed for glasses, whose thermodynamic state has been identified by a single order parameter, that is the fictive temperature,  $T_f$  [6]. This is defined as the temperature at which a glass with a given thermodynamic state would be at equilibrium [7]. Within this approach, once the  $T_f$  is defined, the overall thermodynamic state and any other property of the glass are uniquely determined. Several studies show that the description of the glassy state via a single order parameter is adequate to predict (de)vitrification behavior and physical aging in proximity of  $T_g$  [8]. However, this view has been variously challenged [9–11]. A distribution of  $T_f$  was hypothesized to overcome the inability of a single  $T_f$  to describe the glassy state [10], though this description has been challenged by experiments showing that aging occurs with identical kinetics independently of the mode and its frequency in dynamically heterogeneous relaxation [12,13].

Hence, whether the glass enthalpic state, or equivalently its  $T_f$ , is able to provide a comprehensive description of aging in a simple down-jump experiment remains hitherto

elusive. It is therefore important to investigate aging from the viewpoint of its macroscopic enthalpic state with respect to other observables, delivering further insights on the glass state.

Here, we tackle the problem of defining the state of a glass, investigating the kinetics of aging in different glasses. This is done over a wide temperature and time range for glassy poly(4-chlorostyrene) (P4CIS) (See the Supplemental Material [14] for material and methods description, which includes Ref. [15]). We also investigate aging of other glasses, including nonpolymeric ones, thereby getting insights on the universality of our findings. We employ fast scanning calorimetry (FSC) that allows for following aging at timescales otherwise inaccessible by standard calorimetry (See the Supplemental Material [14] for the description of FSC methods, which includes Refs. [7,16]). Monitoring the aging temperature and time evolution of the glass enthalpy and of devitrification width, we show that significantly below  $T_g$  the time evolution of the former is decoupled from that of the latter, indicating that a single order parameter is insufficient to provide a comprehensive description of aging.

We begin presenting the calorimetric response of P4CIS after isothermal aging at two representative temperatures, 406 and 390 K, after cooling at 1000 K/s; see Fig. 1. Aging at both temperatures shares the common feature of resulting in the typical endothermic peak associated to the recovery of the equilibrated liquid, growing in intensity and shifting to higher temperatures as the aging time increases. Aging at 406 K, just below  $T_f = 413$  K on cooling at 1000 K/s, results in the saturation of the endothermic overshoot after 3 s. Consistently, the time evolution of the recovered enthalpy,  $\Delta H$ , and the devitrification width,  $\Delta T_{\text{dev}}$ , shown in Fig. 1(b), both evolve over time until a plateau after 3 s. Here,  $\Delta T_{\text{dev}}$  is the difference between the onset and offset

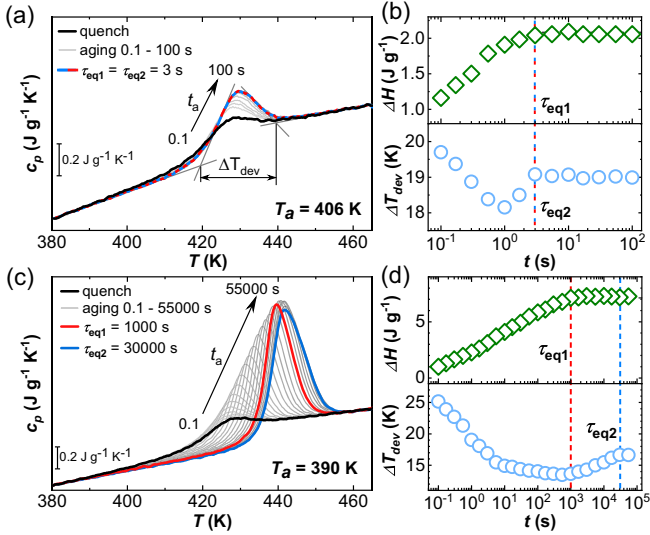


FIG. 1. (a),(c)  $c_p$  scans at  $1000 \text{ K s}^{-1}$  for P4CIS after aging at 406 and 390 K, respectively, and different times. (b) and (d) Corresponding aging time dependent evolution of the recovered enthalpy and glass transition width. Red and blue  $c_p$  scans highlight the aging time at which the glass reaches the enthalpy plateau and stationarity in the glass transition width, respectively.

temperatures,  $T_{\text{on}}$  and  $T_{\text{off}}$ , respectively, of devitrification; see Fig. 1(a) and the Supplemental Material [14] for the description of how  $\Delta T_{\text{dev}}$  is obtained.  $\Delta T_{\text{dev}}$  decreases with time in line with previous reports indicating narrowing of the relaxation spectrum during aging [17]. The  $\Delta H$  at the plateau corresponds to the enthalpy expected at equilibrium extrapolating the supercooled liquid line; see the Supplemental Material [14], Fig. SM2. For aging at 390 K, enthalpy evolves with time until a plateau after  $\tau_{\text{eq1}} = 1000 \text{ s}$  [red line in Fig. 1(c)] that, similarly to aging at 406 K, corresponds to the enthalpy of the extrapolated liquid line; see Fig 1(d), upper panel. However, differently from aging at 406 K, on aging for times longer than 1000 s, further isoenthalpic evolution of the devitrification pattern is observed until specific heat scans overlap for times  $\tau_{\text{eq2}} \geq 30000 \text{ s}$  [blue line, Fig. 1(c)]. Specifically, a broadening of the devitrification endotherm, accompanied by a simultaneous minor decrease in maximum intensity and shift to higher temperatures, is observed. An overview of the aging behavior at 390 K is depicted in Fig 1(d), providing the time dependent evolution of both  $\Delta H$  and  $\Delta T_{\text{dev}}$ .

Extensive characterization of the aging evolution of  $\Delta H$  and  $\Delta T_{\text{dev}}$  over a wide time and temperature range below  $T_g$  is reported in Fig. 2. As expected, decreasing the aging temperature results in an increase of  $\Delta H$  at equilibrium [Fig. 2(a)] and the associated time required to reach equilibrium,  $\tau_{\text{eq1}}$ . For all explored temperatures, the  $\Delta H$  values taken at the plateau equal those expected at equilibrium; see Fig. SM2 of the Supplemental Material [14]. Interestingly,  $\Delta T_{\text{dev}}$  exhibits nonmonotonic behavior:

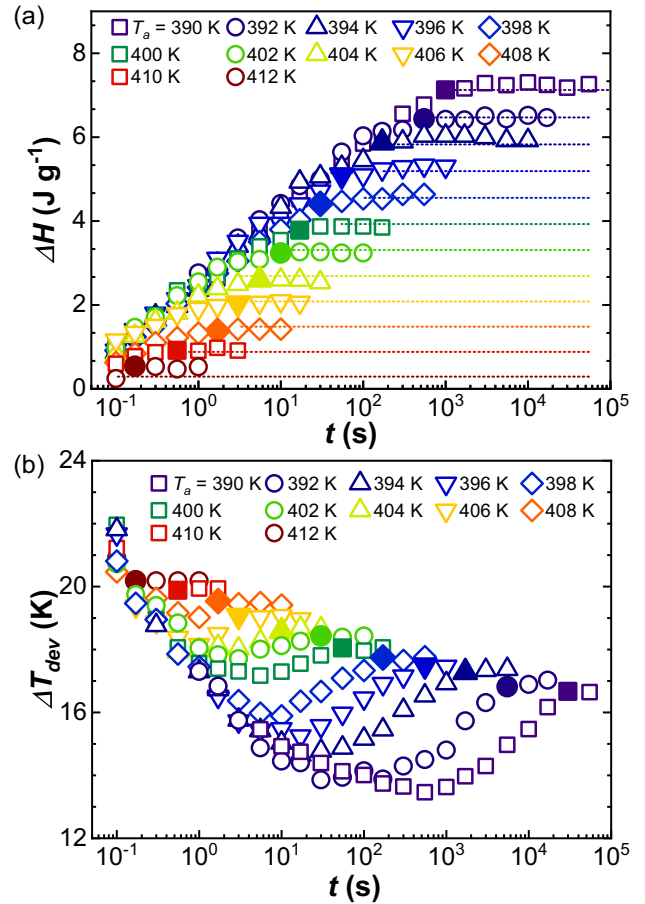


FIG. 2. Aging kinetics in a wide temperature interval followed by changes of (a) enthalpy recovery and (b) glass transition width over time. Full symbols mark time at which the steady-state values are reached and dashed lines in panel (a) the enthalpy needed to reach the equilibrium liquid at the indicated  $T_a$ .

in all cases, it decreases in the first stages of aging and increases up to the equilibrium value at longer times. Similarly to  $\tau_{\text{eq1}}$ , the time to reach a steady-state value in  $\Delta T_{\text{dev}}$ ,  $\tau_{\text{eq2}}$ , increases with decreasing aging temperatures. However, while close to  $T_g$  the two timescales essentially coincide,  $\tau_{\text{eq2}}$  exhibits increasingly larger values with decreasing aging temperature with respect to  $\tau_{\text{eq1}}$ .

The kinetics of aging reported in Fig. 2 from two different viewpoints allows one to extract the temperature dependence of equilibration times,  $\tau_{\text{eq1}}$  and  $\tau_{\text{eq2}}$ . This is shown in Fig. 3, where, beside  $\tau_{\text{eq1}}$  and  $\tau_{\text{eq2}}$ , the temperature dependence of the main  $\alpha$  relaxation time,  $\tau_{\text{mol}}$ , from literature data by broadband dielectric spectroscopy [18] and measured in the present study by calorimetry via step response analysis [19,20] (see the Supplemental Material [14] for the description of step response protocols) is reported too. The temperature dependence of the two equilibration times mimics that of  $\tau_{\text{mol}}$  at relatively high temperatures ( $T_a > \sim 406 \text{ K}$ ). Here it is worth mentioning that, while the temperature dependence of the two  $\tau_{\text{eq}}$  is the

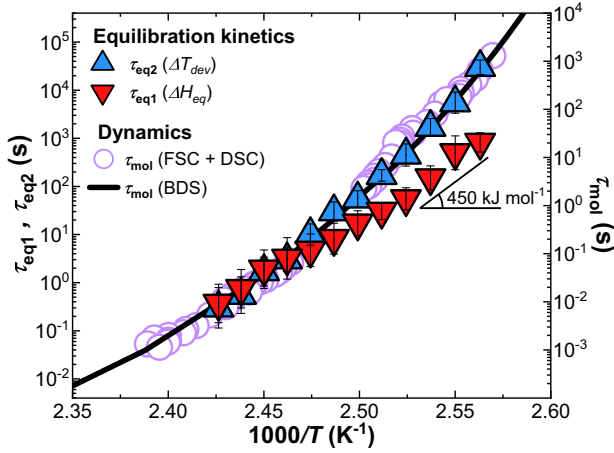


FIG. 3. Temperature dependence of aging kinetics. Equilibration time for enthalpy ( $\tau_{eq1}$ ) and glass transition width ( $\tau_{eq2}$ ) as a function of inverse temperature. For comparison, P4CIS  $\tau_{mol}$  from step response calorimetry measurements (see the Supplemental Material [14]) and BDS, taken from Ref. [18] is displayed.

same as that of  $\tau_{mol}$ , the absolute times are different. The difference  $\tau_{eq}$  and  $\tau_{mol}$  quantifies the efficiency of the latter to restore equilibrium [18,21]. Differently from the high temperature regime, below  $T_a \sim 406$  K,  $\tau_{eq1}$  exhibits milder temperature dependence with respect to both  $\tau_{eq2}$  and  $\tau_{mol}$ . This result indicates that the kinetics of physical aging depends on the monitored observable.

While the present work reports a detailed investigation on the kinetics of physical aging of P4CIS, we extended our analysis to three additional glassy polymers spanning a wide range of  $T_g$ , poly(1-4 cyclohexane di-methanol) (PCDM), poly(ethylene terephthalate) (PET), and polyarylate (PAR), plus two small molecule glasses to rule out polymer specific effects: phenolphthalein dimethyl ether (PDE) and 1,1-bis(4-methoxyphenyl)cyclohexane (BMMPC) (See the Supplemental Material [14] for information on these glasses and aging protocols, which includes Refs. [22,23]). We focus on one aging temperature in the regime considerably below  $T_g$ , although a detailed analysis over a wide aging temperature range is reported for PDE (see the Supplemental Material [14]). Aging data for PCDM, PDE, and BMMPC were taken from previous studies [24,25], whereas those for PET and PAR have hitherto not been reported elsewhere. Figure SM7 of the Supplemental Material [14] shows the evolution of specific heat scans on heating at 1000 K/s after aging in a wide aging time range and at the indicated aging temperatures. In all cases, and in ways completely analogous to P4CIS, equilibrium in the  $\Delta H$  takes place in timescales significantly shorter than those needed to approach the steady-state value of  $\Delta T_{dev}$ . Furthermore, similarly to P4CIS, for PDE  $\tau_{eq1}$  exhibits milder temperature than  $\tau_{eq2}$  and  $\tau_{mol}$  (see Fig. SM8 of the Supplemental Material [14]). Hence, the decoupling between  $\tau_{eq1}$  and

$\tau_{eq2}$  is a common feature in glasses of different nature,  $T_g$ , and chemical structure.

The study of physical aging of glasses relies on monitoring the time evolution of a given observable. The latter can be chosen among all properties sensitive to the time dependent nature of the glass. These can be categorized in two main groups: (i) those sensitive to changes in the glass molecular-atomic mobility and its distribution, as done following the aging time dependence of the mechanical [5] or dielectric [26] susceptibility (or modulus), or in measurements where the aging time dependent autocorrelation function is monitored [27,28] and (ii) those where a first order thermodynamic (or related to) property is monitored during aging [3,4].

Calorimetry is typically employed to monitor the aging time evolution of the glass enthalpy [16,29]. Our study goes beyond this mere information, conveying information on devitrification kinetics, related to the distribution of relaxation times in the glass and parametrized via  $\Delta T_{dev}$ . Relatively short aging times and/or high temperatures result in complete consistence between enthalpy and  $\Delta T_{dev}$  reduction, the latter indicating homogenization of glass dynamics. However, our results show unequivocally that, significantly below  $T_g$ , once after a certain aging time the glass enthalpy attains the equilibrium value, further evolution takes place in the way the glass devitrifies. Specifically, long term aging in isoenthalpic conditions indicates the evolution toward a dynamically more heterogeneous system, as indicated by the increase of  $\Delta T_{dev}$ . Interestingly, this increase depends on the kind of investigated glass and weakly correlates with the glass  $T_g$  (see Fig. SM9 of the Supplemental Material [14]). Importantly, inspection of previous results by standard DSC, presented in a dedicated figure of the Supplemental Material [14] (Fig. SM10), shows an analogous decoupling between enthalpy relaxation and devitrification kinetics, indicating that this outcome is independent of the applied heating rate [30,31].

The nonmonotonic aging time evolution of  $\Delta T_{dev}$  is consistent with experiments and simulations showing analogous results on the temporal evolution of density and enthalpy fluctuations in different glasses, consisting of an initial increase in glass homogeneity followed by increased heterogeneity at longer times [32,33]. Consistently, a direct determination of the glass mobility via stress relaxation and nanoindentation experiments in different metallic glasses and a polymer showed a decrease of the time dependence of the glass dynamic heterogeneity in the first stages of aging followed by an increase at longer times [34]. This behavior has been explained as resulting from the sequential equilibration [17,35] due to fast relaxing tails at the initial stages of aging, making the glass relaxation spectrum more narrow, followed by full equilibration of slow relaxing tails, resulting in a final broadening [32,33].

Our study shows that, a single order parameter, that is, the glass thermodynamic state, is enough to provide a complete description of glass equilibration close to  $T_g$  [8]. In these conditions, the timescale of enthalpy equilibration coincides with that to attain stationarity in  $\Delta T_{\text{dev}}$ , implying a one-to-one correlation between the two magnitudes [36]. However, when physical aging is carried out significantly below  $T_g$ , the glass enthalpic state fails to provide a complete description of glass equilibration, and a second order parameter is required, the latter accounting for the molecular-atomic mobility in the glass and its heterogeneity. The inability of the macroscopic enthalpic state to provide a comprehensive description of the glass has been highlighted in studies where glasses obtained under different kinetic routes with identical enthalpies exhibited different pathways of devitrification [37] and properties, ranging from electrical resistivity to the thermal expansion coefficient [38]. Furthermore, the presence of two-order parameters is consistent with recent findings on a metallic glass showing nonmonotonic temperature dependence of the glass hardness and decoupling from the enthalpic state [39]. Similarly, a decoupling between the enthalpic state and the glass structural and mechanical properties was found in a metallic alloy obtained under a variety of thermal protocols [40]. Apart from the analogy with the outcome of our work, it is noteworthy that our findings, showing that the time evolution of the enthalpy and that of a magnitude related to the glass dynamic heterogeneity follow different kinetics paths, are unprecedented.

Within the two-order parameter description, it is noteworthy that the timescales of approach to equilibrium of the macroscopic enthalpy and that of  $\Delta T_{\text{dev}}$  exhibit a splitting below a certain aging temperature, as detailed for P4CIS and PDE; see Fig. 3 and Fig. SM8, respectively. The long timescale,  $\tau_{\text{eq}2}$ , at which stationarity is achieved for  $\Delta T_{\text{dev}}$ , follows identical temperature dependence to that of the  $\alpha$  relaxation [18]. In contrast, achievement of equilibrium of the enthalpy takes place via  $\tau_{\text{eq}1}$ , exhibiting milder temperature dependence. This result must be put in the context of recent findings in a variety of glasses, including polymers [24,41–43], metallic [44–46], and chalcogenide [47,48] glasses—summarized in a recent review [21]—where multiple timescales of equilibration were identified, each conveying the glass to a relative free energy minimum. These reports, in analogy with our study, unveil the presence of a fast mechanism of equilibration, whose activation is milder than that of the  $\alpha$  relaxation. This mechanism conveys the glass to an intermediate plateau, with enthalpy larger than that at equilibrium. Importantly, our results show that, at temperatures higher than those required to observe a splitting in two steps of the equilibrium recovery, the glass already displays two timescales of equilibration. This is consistent with recent reports showing a transition from the fast relaxation dominated regime, often addressed as  $\beta$  relaxation regime, observed at the early stages of aging and/or at low annealing temperatures,

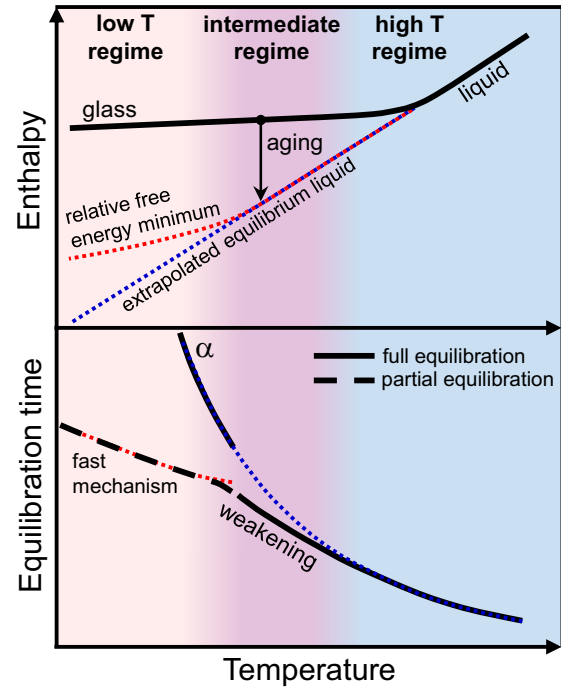


FIG. 4. Schematic representation of different temperature regimes of glass aging from the viewpoint of the enthalpy (a) and equilibration time (b).

to the long aging time behavior, where the  $\alpha$  relaxation dominates glass equilibration [25,37,49–51].

The results of our study, combined with the previous understanding of physical aging, allows one to distinguish the kinetics of physical aging in three main regimes, as depicted in Fig. 4. In the high aging temperature regime, in proximity of  $T_g$ , glass aging takes place with kinetics mediated by a single,  $\alpha$  relaxation related, equilibration mechanism, irrespective of the observable, enthalpy, or devitrification width. At lower aging temperatures, hereby addressed as the “intermediate regime,” enthalpy equilibration still exhibits monotonous aging time dependence. However, while full equilibration, denoted by  $\Delta T_{\text{dev}}$  stationarity, still takes place with kinetics associated to the  $\alpha$  relaxation, a new fast timescale emerges underlying enthalpy equilibration. Finally, in the low aging temperature regime, way below  $T_g$ , the timescale duality observed in the intermediate regime evolves into a split in two steps of enthalpy evolution, with the faster step conveying the glass to a relative free energy minimum with enthalpy in excess with respect to the extrapolated supercooled liquid.

As discussed, the fast timescale of glass equilibration exhibits milder temperature dependence than that of the  $\alpha$  relaxation with activation energy of  $\sim 450$  kJ/mol (see Fig. 3). The same applies to glasses exhibiting two steps in enthalpy relaxation, where the first step display kinetics with similar activation energy [24,41,52]. However, it is worth pointing out that, if aging is conducted way below  $T_g$ , where the  $\alpha$  relaxation is completely inactive, the first step of

glass equilibration exhibits reduced activation energy, approaching values as low as  $\sim 100$  kJ/mol, as observed in confined polymers [53]. The molecular-atomic mechanism responsible for glass equilibration in the low temperature regime could be addressed as generically originating from  $\beta$  relaxation [49,50]. However, in the case of P4CIS, this appears to be too fast with respect to  $\tau_{\text{eq1}}$  ( $\tau_{\beta} = 10^{-2}$  s vs  $\tau_{\text{eq1}} = 1000$  s at 390 K) and its activation energy ( $\sim 120$  kJ mol $^{-1}$ ) [54] considerably smaller than that of  $\tau_{\text{eq1}}$ . Here, we point out that, whatever its origin, the fast mechanism must bear potential in glass equilibration, as for instance recently demonstrated for a slow Arrhenius process identified in both polymeric [18] and small molecules [55] glasses, whose long relaxation time above  $T_g$  allows one to capture the long aging tail evolution in certain conditions [56], including large temperature up jumps [51].

In conclusion, we have tackled the long standing issue of how a glass brought out of equilibrium on cooling through the glass transition from the supercooled liquid state equilibrates. Specifically, instead of focusing on a single observable, exploiting the capability of FSC, we have followed the aging time evolution of both the glass enthalpy and the way it devitrifies on heating to the supercooled liquid in terms of glass transition width,  $\Delta T_{\text{dev}}$ . Aging close to  $T_g$  results in a complete coupling between the time evolution of the enthalpy and  $\Delta T_{\text{dev}}$ , with the latter observable indicating the evolution toward a dynamically more homogeneous glass. In contrast, aging at temperatures significantly below  $T_g$  shows that enthalpy equilibration takes place in shorter times than that of  $\Delta T_{\text{dev}}$ . The latter, while evolving toward a more homogeneous glass at short aging time, exhibits an enhancement of dynamic heterogeneity in the last stages of aging.

*Acknowledgments*—We wish to acknowledge Grant No. PID2021-123438NB-I00 funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe”; the financial support of Eusko Jaurlaritza, code IT1566-22; Grant No. PID2020-114506 GB-I00 funded by the Spanish Minister of Science and Innovation; and TED2021-129457B-I00 funded by the Spanish Minister of Science and Innovation.

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