

Comment on “Anomalous structural recovery in the near glass transition range in a polymer glass: Data revisited in light of temperature variability in vacuum oven-based experiments”

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Abstract

Recent efforts, fostered by a pioneering work by us, have shown the of multiple steps in the recovery of equilibrium of glasses. Jin and McKenna raise concerns regarding the validity of such scenario alleging that the multiple recovery steps would be an artifact arising from poor temperature control in the oven used for isothermal glass equilibration. We critically discuss Jin and McKenna arguments from both the viewpoints of scrutinizing previous literature data and that of the temperature control in the oven. In doing so, we provide compelling arguments that Jin and McKenna conjectures are unjustified and point out the need for efforts to describe glass dynamics significantly below the glass transition temperature, T_g , by accounting for the presence of different relaxation mechanisms active in glass equilibration.

KEYWORDS

glasses, physical aging, structural recovery

A recent paper by Jin and McKenna^[1] discusses on the presence of multiple steps in the approach to equilibrium of glasses, often addressed as physical aging.^[2,3] This scenario indicates the existence of mechanisms of equilibration beyond the main α relaxation, generally associated to the glass transition. Specifically, Jin and McKenna^[1] raise severe concerns on the validity of our seminal work addressing the presence of multiple steps,^[4] in the light of apparently contradicting results by Koh and Simon^[5] on a single polystyrene (PS) sample with one molecular weight at one single aging temperature showing a single step. In particular, according to Jin and McKenna,^[1] the presence of multiple steps in the approach to equilibrium would be the result of an artifact originating from poor

temperature control in the oven used to anneal glassy samples.

First of all, it is worthy of remark that a direct test of the correct functioning of our oven by Jin and McKenna^[1] has never been carried out. Hence, as a due premise, all the discussion reported in their manuscript must be considered as a mere hypothesis. Furthermore, in this comment, we provide compelling arguments that the issues raised by Jin and McKenna^[1] are completely unjustified from both the viewpoint of the analysis of available literature data on equilibrium recovery of glasses and that of technical aspects of temperature control.

A significant part of Jin and McKenna work^[1] recalls renowned results by Kovacs^[6] and more recent ones by

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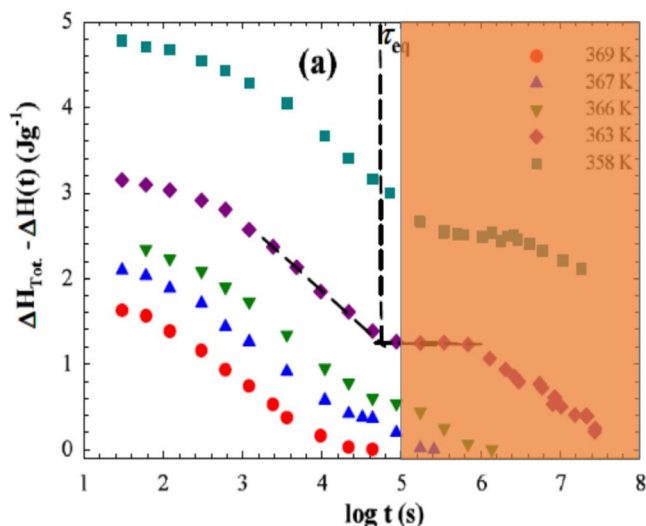


FIGURE 1 Enthalpy recovery data taken from Cangialosi et al.^[4]

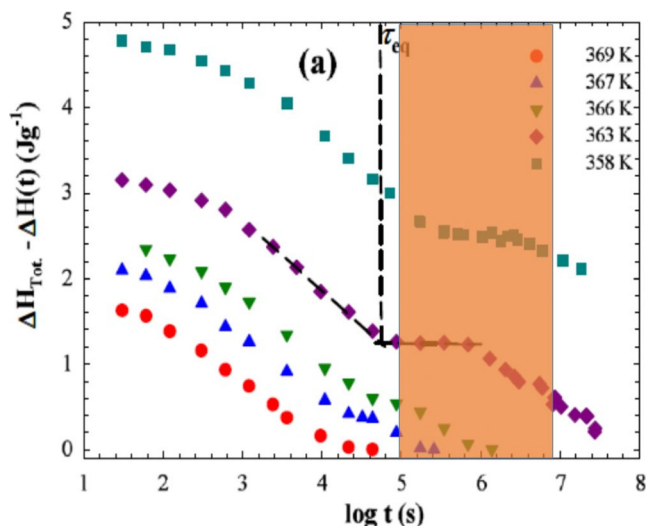


FIGURE 2 PS enthalpy recovery data taken from Cangialosi et al.^[4]

Czerniecka-Kubicka et al.^[7] showing a single decay toward equilibrium. Regarding Kovacs aging data, these are volume recovery results never extending over 10^5 s aging time. There exists no theoretical justification to extend these data up to 10^9 s by building a master curve obtained making an a priori assumption on the validity of aging time–temperature superposition, that is, thermorheological simplicity, as done by Jin and McKenna^[1] (figure 2 of that paper). Hence, let us now consider our results on PS,^[4] that is the polymer for which an apparent discrepancy with Koh and Simon^[5] results would exist, after truncating the aging time at 10^5 . This is shown in Figure 1. As can be observed, if aging data are considered until 10^5 s, one should conclude that a single decay exists.

Hence, there exists no discrepancy with Kovacs results.^[6] The aging time–temperature superposition shown in figure 2 of Jin and McKenna,^[1] extending data up to 10^9 s, would be acceptable only if the single decay scenario was true, but this cannot be proved by data limited to only 10^5 s.

A second attempt by Jin and McKenna^[1] to confute our results^[4] recalls enthalpy recovery data by Czerniska-Kubicka et al.^[7] These data are extended up to 1 year aging and, therefore, could be a more stringent test with respect to Kovacs data.^[8] Unfortunately, if the analogy with our work^[4] should be tested, data of Czerniska-Kubicka et al.^[7] lack the decisive aging time regime, that is, the one from 10^5 and 10^7 s. If data in this range are excluded in Cangialosi et al.^[4] study, as shown in Figure 2, the existence of the double step recovery would also remain unseen. Consequently, results from Czerniska-Kubicka et al.^[7] cannot be used to prove nor disprove the double step decay scenario. Furthermore, Jin and McKenna,^[1] to strengthen the single decay scenario, quote another work by Czerniska-Kubicka and Pyda,^[9] where enthalpy recovery of poly(L-lactic acid) (PLLA) is monitored. Panel b of figure 22b of Czerniska-Kubicka and Pyda,^[9] shows enthalpy evolution at 45°C for aging times up to 10^5 s. Despite the relatively short aging time, these enthalpy recovery data seem to indicate a plateau between 3×10^3 and 2×10^4 s aging, followed by further evolution at larger aging times. Hence, Czerniska-Kubicka and Pyda^[9] study on PLLA rather supports the two step decay scenario of equilibrium recovery.

While selecting some works reporting the single step scenario, Jin and McKenna^[1] fail to provide a comprehensive overview of structural recovery data collected along decades. These can be divided into four groups: (1) those carried out close to the glass transition temperature, T_g , showing a single step decay toward the final equilibrium; (2) experiments conducted significantly below T_g showing only partial recovery without sign of any plateau; (3) experiments also conducted way below T_g but for long enough aging time that a plateau with partial equilibrium recovery is attained; (4) those where two steps are identified. The first two groups of experiments do not provide any discriminant to decide whether the two steps recovery scenario is a real fact. In contrast, there exists overwhelming experimental evidence indicating the presence of the first plateau, with partial enthalpy recovery in experiments conducted significantly below T_g . A list of works containing these experiments is provided here below: Bauwens-Crowet and Bauwens^[10] on polycarbonate (PC); Brunacci et al.^[11] on PS; Cowie et al.^[12] on poly(vinyl acetate) (PVAc); Dueñas et al.^[13] on styrene–acrylonitrile (SAN) copolymer; Hutchinson^[14] on PVAc (in this case, the partial recovery is evident once the value of the sample mass reported in the article is used to convert heat flow

rates into specific heats); Andreozzi et al.^[15,16] on poly(methyl methacrylate) (PMMA); McGonigle et al.^[17] on PS; Simon et al.^[18] on germanium-selenide glasses; Tanaka et al.^[19] on PS; Cangialosi et al.^[20] on different high T_g polymers. Interestingly even the same authors raising concerns^[5] in the presence of an intermediate plateau with partial enthalpy recovery show evidence for its existence. In Simon et al.,^[18] the enthalpy recovery of germanium-selenide glasses is investigated. In figure 2 of that work, the absolute specific heat capacities are shown for these glasses with different compositions. If for instance one considers the glass labeled “2.1” (but the same arguments are valid for all other compositions), this exhibits $\Delta C_p(T_g) = 0.15 \text{ J/g K}$. This implies that at $T_g - 15 \text{ K}$ the total recoverable enthalpy is (approximately) $\Delta C_p(T_g) * 15 = 2.25 \text{ J/g}$. However, in figure 7c of Simon et al.,^[18] the glass labeled “2.1” only recovers $\Delta H = 1.5 \text{ J/g}$ to a plateau. This is one-third smaller than the total recoverable enthalpy. Even the authors of that article recognize this with the following statement: “at the lowest two aging temperatures, we observe that data deviate from the expectation with the observed ΔH_a , being less than that predicted.” Hence, this result can only be explained recognizing the existence of the two steps recovery.

Studies showing the two steps decay are less numerous and the reason is straightforward: in most cases either the annealing temperature is too close to T_g and, therefore, the two steps are merged or convoluted; or the annealing temperature is so low that the second step cannot be observed in experimentally accessible time scales due to the fact the α relaxation, to which this step is associated, steeply increases to astronomical time scales not far from T_g . Still, apart from our work,^[4] importantly there exist several reports showing the existence of multiple steps of equilibrium recovery. These reports are on a wide variety of glass formers: low molecular weight organic compounds,^[21] chalcogenide glasses,^[22,23] metallic glasses,^[24–26] glassy polymers^[27,28] and very recently the most simple polymeric glass former, that is, selenium.^[29] The latter study is especially relevant as the aging time dependence of the glass enthalpy was monitored for up to 40 years. This allows separating the two-time scales of equilibrium recovery at aging temperatures significantly below T_g . Another study, carried out closer to T_g showed that the shape of equilibrium recovery behavior, though not showing any evident non-monotonous pattern, was better fitted by two-time scales.^[30]

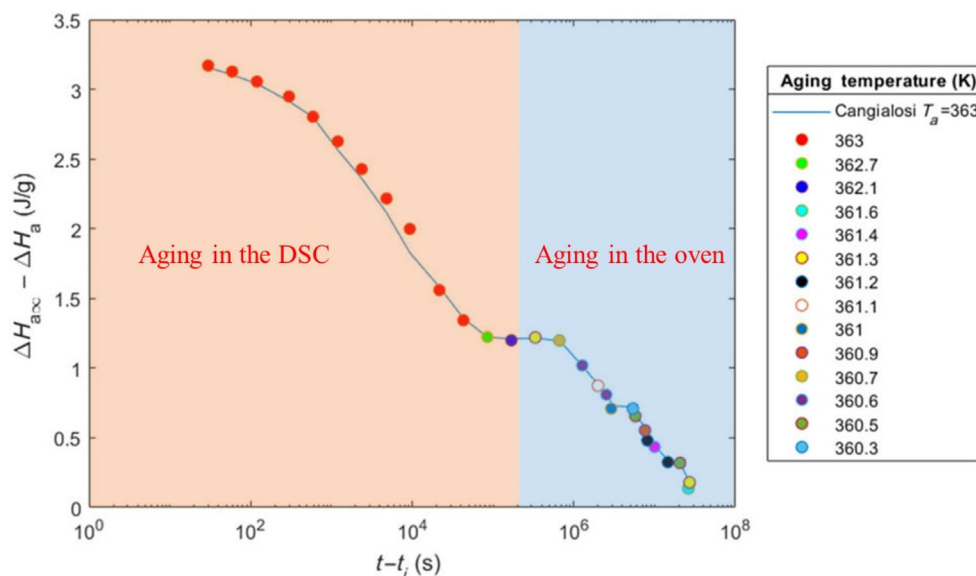
The presence of multiple steps of equilibrium recovery underlines the presence of different mechanisms of equilibration. While, as previously explained, highlighting their simultaneous presence is a hard task in isothermal aging, isochronal measurements, for instance heating at a constant rate after aging way below T_g , helps to unveil the existence of the fast mechanism of

equilibration, that is, the one relevant for the first decay in isothermal experiments. As a general feature, studies conducted in this way show a broad endotherm at temperatures significantly below T_g . This was shown in a wealth of experiments on a variety of glasses.^[20,25,31–39] Importantly, in the latter study, by Caruthers and coworkers,^[39] the low temperature endotherm exhibited by a polymer glass aged way below T_g was accompanied by thermo-rheological complexity, as proved by mechanical experiments. The authors concluded that equilibration must take place accounting for two processes, which is in line with the existence of two-step decay shown by us in isothermal aging.^[4] A similar conclusion was attained by Cassidy et al.,^[40] who, by magnetically polarized neutron scattering experiments, showed that in aging way below T_g diffusion must be excluded differently from aging close to T_g . The low temperature endotherm was actually already shown long ago by Hodge and coworkers.^[41] Very importantly, the authors attempted to model specific heat scans showing this feature employing the Tool-Naraswamy-Moynihan (TNM) model, that is, the same model employed by Jin and McKenna,^[1] and found unphysically small stretching exponents, β_{KWW} , and/or non-linear parameters, x . They concluded that the TNM model, with a single time scale, was inadequate to describe specific heat scans exhibiting the low temperature endotherm. The existence of two-time scales for structural recovery, as indicated by the two steps recovery,^[4] provides a natural explanation to the inadequacy of the TNM model with a single time scale.

The existence of multiple mechanisms of equilibration is also highlighted in renowned experiments by Greiner and Schwarzl.^[42] On cooling slowly enough to separate the different time scales corresponding to the different mechanisms of equilibration, they showed that specific volume versus temperature plots exhibit different kinks, each corresponding to the loss of equilibrium with respect to each free energy minimum. Indirect proofs of the presence of a second low temperature mechanism of equilibrium recovery are provided by enthalpy recovery experiments on semi-crystalline polymers,^[43,44] where the T_g shift with respect to the fully amorphous system, modifies the α process driven aging behavior close to T_g . In contrast, aging way below T_g proceeds with the same behavior irrespective of the system crystallinity, indicating that a mechanism insensitive to the modification of the α relaxation triggers equilibrium recovery in this regime.

Apart from the previously discussed neglect of the wealth of experimental work showing multiple mechanisms of equilibration, important concerns must be raised on the purported technical inaccuracies suggested by Jin and McKenna^[1] on temperature control in the oven. First of all, the authors report private communications from both Koh et al.^[5] and Czerniecka-Kubicka

FIGURE 3 PS enthalpy recovery data at 363 K taken from Cangialosi et al.^[4] showing that samples aged in the DSC, that is, below at maximum 48 h, already show a plateau in the enthalpy



et al.^[7] regarding the temperature control in their ovens. This information goes beyond that reported in the public manuscripts. Regrettably, Jin and McKenna^[1] fail to request similar information to us beyond those contained in our article.^[4] They would have learnt that DSC pans in the oven were located in direct contact with a metal block, with mass much larger than that of the DSC pan plus the sample, that a thermometer was placed beside them and, therefore, temperature stability was continuously monitored. The maximum observed temperature variation was ± 0.5 K. We used an oven from Heraeus Instruments, which is different from the Isotemp Vacuum Oven Model 281A from Fisher Scientific, that Jin and McKenna^[1] use to show temperature gradients. Experiments in the DSC, as customary, were conducted in nitrogen flux that guarantees temperature stability. Even only considering the information reported in our manuscript,^[4] the argument of a poor temperature control does not hold. Though control experiments in the DSC were conducted even for larger times, that is, up to several months—in this case, within the experimental error (± 0.05 J/g) we obtained the same results as in the oven—we report 48 h as the maximum time for aging experiments in the DSC, corresponding to about 2×10^5 s. In contrast, figure 8 of Jin and McKenna article^[1] alleges an uncontrolled temperature evolution, which within the authors approach would happen in the oven, already after 2×10^4 s. Hence, according to the authors the temperature drop would already begin in the DSC and a coherent drop would take place in the oven. To confront the experimental protocol we used with the scenario drawn by Jin and McKenna,^[1] we have reported here figure 8b of their work highlighting the two zones where, just accounting for the reported 48 h aging in the DSC in our work,^[4] aging in the DSC and in the oven are carried

out (Figure 3). We note that data corresponding only to DSC results already show the existence of a plateau. Hence, Jin and McKenna hypothesis would depict a synchronized temperature drop in the DSC and in the oven. Furthermore, that a gradual temperature drop would take place in the oven during time and in a systematic way for all experiments is also a peculiar scenario (see different panels of figure 8 of Jin and McKenna^[1] work).

Altogether, Jin and McKenna^[1] discuss apparently different results between our work^[4] and that of Koh and Simon.^[6] However, apparent discrepancies among experiments do not necessarily imply that one of the two is wrong. The first thing to do should be seeking for differences between the two experiments. Careful inspection of the materials subjected to aging indicates that in our work a PS with very narrow distribution of molecular weights was employed,^[4] while Koh and Simon^[5] used the same polymer but with a wide molecular weight distribution, with low molecular weight tails that enhance dynamic heterogeneities. In line with this hypothesis, we note that our experiments also involved a mono-distributed PS with low molecular weight, which displayed aging behavior considerably different from the high molecular weight PS. We conclude that the distribution of molecular weights is one potential source of discrepancy not requiring any insinuation of experimental inaccuracy on both sides. Notwithstanding the inadequacy of Jin and McKenna^[1] arguments to confute the double step decay scenario, in a completely general framework, that is, not discussing any specific experiment, the TNM model could be used to address how poor temperature control could affect the assessment of equilibrium recovery kinetics. Beside the simulation of a double step recovery caused by gradual temperature drop in the oven, the opposite can be done. Specifically, a single

step recovery could be simulated by assuming an increase in temperature in the oven, after implementing the two-time scales of structural recovery in the TNM model.

As a final general remark, focusing on a single apparent controversy—which as previously detailed should not even exist—could be detrimental for advancing our understanding of glass dynamics deep in the glassy state. Way more beneficial would be trying to understand the overwhelming experimental activity showing the existence of multiple mechanisms of equilibration; how this complex behavior can affect aspects of extraordinary importance such as vitrification,^[45] crystal nucleation,^[46,47] and ionic conductivity^[48]; and the development of theoretical approaches able to capture this phenomenology.^[49–52]

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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