

Reaching the Ideal Glass in Polymer Spheres: Thermodynamics and Vibrational Density of States

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The existence of an ideal glass and the resolution to the Kauzmann paradox is a long-standing open question in materials science. To address this problem, we exploit the ability of glasses with large interfacial area to access low energy states. We submit aggregates of spheres of a polymeric glass former to aging well below their glass transition temperature, T_g ; and characterize their thermodynamic state by calorimetry, and the vibrational density of state (VDOS) by inelastic neutron scattering (INS). We show that, when aged at appropriate temperatures, glassy spheres attain a thermodynamic state corresponding to an ideal glass in time scales of about one day. In this state, the boson peak, underlying the deviation from the Debye level of the VDOS, is essentially suppressed. Our results are discussed in the framework of the link between the macroscopic thermodynamic state of glasses and their vibrational properties.

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A liquid can be cooled down below its melting temperature, provided that large cooling rates are used to avoid crystallization. Conventional supercooled liquids generally exhibit a thermodynamic state independent of the thermal history [1]. Further cooling leads to the formation of a glass, whose thermodynamic state profoundly depends on the way this is formed and on its thermal history [2]. The temperature at which the supercooled liquid loses equilibrium—the so-called glass transition temperature, T_g —which defines the potential energy of the glass (see Fig. 1), progressively decreases with the cooling rate. Once in the glassy state, spontaneous evolution towards low energy states takes place. Accessing these states in glasses may convey insights of utmost importance to unveil the nature of the glass transition.

Activity in this sense was stimulated long ago by the analysis of Kauzmann on several glass formers [3]. He noticed that, due to its large specific heat, the entropy of a supercooled liquid decreases on cooling faster than that of the corresponding crystal. Hence, there would be a temperature, addressed as the Kauzmann temperature, T_K , at which the supercooled liquid and the crystal entropies match. The existence of a supercooled liquid below T_K would imply an entropy catastrophe with the unphysical scenario of a liquid having smaller entropy than that of the corresponding crystal. To avoid this paradoxical scenario, it has been proposed [4–6] and largely debated [7–14], that a true second order thermodynamic transition, the so-called “ideal” glass transition, at T_K would take place. The existence of such a transition would mean the emergence of an ideal glass residing at the bottom of Goldstein’s free

energy landscape [15], excluding the crystal occupying the ultimate minimum (see Fig. 1). The thermodynamic state of a glass can be defined via the so-called fictive temperature, T_f [16], the temperature of the intercept of the extrapolated

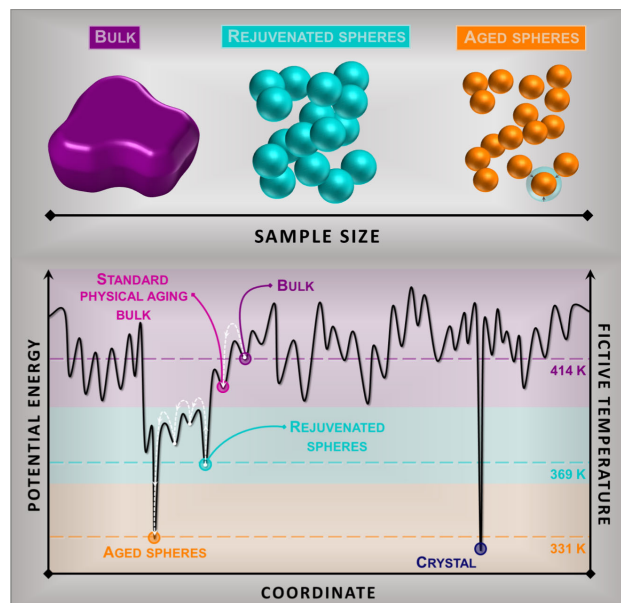


FIG. 1. Schematic representation of the potential energy landscape and the corresponding T_f for bulk and spheres glasses. Bulk, rejuvenated, and aged spheres are located at high, intermediate, and low energetic minima in the landscape, respectively. The scheme shows how aging bulk glasses only allows limited energy decrease, whereas massive decrease takes place upon aging spheres.

glass and supercooled equilibrium lines. $T_f \approx T_K$ defines the thermodynamic state of an “ideal glass,” while $T_f \approx T_g$ that for a “fresh glass,” obtained by cooling at a certain rate.

Attaining information on the ideal glass transition is hampered by the transformation of the supercooled liquid into a glass. Hence, reducing the energy requires the spontaneous evolution of the glass towards the equilibrium supercooled state, a phenomenon known as physical aging [17–19]. However, accessing low energies in bulk glasses by physical aging generally involves unfeasibly large time scales. For instance, glassy amber aged for millions of years [20,21] exhibits T_f significantly lower than T_g but still well above T_K . Aging bulk glasses over laboratory time scales only allows limited reduction of the glass energy (see Fig. 1).

Recently other routes have been explored to access low energy states [22,23]. Among them, a recently developed one relies on the ability of glasses with large free interface [24] to reach equilibrium in time scales way shorter than bulk glasses [25,26]. This is for instance evidenced by the finding of accelerated aging found in glasses of different nature having in common the large amount of free interface [27,28]. The efficiency of these systems to approach or maintain equilibrium has been explained accounting for models based on free volume holes diffusion [29,30]; whose evidence was directly verified in colloidal glasses [31]. In this way, different polymeric glasses have been shown to exhibit T_f reductions as large as several tens of Kelvin [32] and in one specific case, that is, 30 nm thick polystyrene films as low as $T_f \approx T_K$ [12], thus creating glasses that by standard aging would take geological time scales to attain these low T_f .

Apart from the thermodynamic view, the achievement of low energy glasses has generated intense debate on how the vibrational density of state (VDOS) of a glass depends on its thermodynamic state [33]. The typical signature of the VDOS in disordered systems, including glasses, is the presence of the boson peak, that is, a low frequency excess of the VDOS with respect to the Debye level, generally found in crystals [34]. The boson peak has been interpreted either as arising from (quasi)localized modes [35] or being associated with random fluctuations of force constant originating from the intrinsic disordered nature of glasses [36]. Several studies on low T_f glasses, including amber aged during geological time scales [21,37] and vapor deposited glasses [38,39], show significant depletion of the boson peak, which is explained by the decrease in the disorder of the glass. Hence, a question of utmost importance is whether the absence of disorder originating from the vanishing configurational entropy—the entropy depleted of its vibrational component—of the ideal glass with $T_f = T_K$ would result in the complete fading of the boson peak, in analogy to crystals with zero configurational entropy.

In this work, we exploit the ability of glasses with a large amount of free interface to access low energy states and

characterize their VDOS by inelastic neutron scattering (INS) (see Supplemental Material [40], which includes Refs. [41–44]). We magnify the free interfacial area by employing aggregates of spheres made of a polymeric glass former, poly(4-*tert*-butyl styrene) (PtBS) with diameter ≈ 150 nm. This is a model system of glass former chosen for its ability to form morphologically stable spheres. However, it is worth to remark that the approach based on enhancing the free interfacial area may be in principle extended to a diverse range of glass formers, provided that equilibrium bulk behavior is maintained. This is true in those cases where the typical length scale of the sample is large enough that the equilibrium thermodynamics is essentially bulklike. Spheres with diameter 150 nm fulfil this criterion as extensively discussed in the Supplemental Material [40], which includes Refs. [45–58]. Characterizing the time evolution of the enthalpy, that is, the energy at constant pressure, in terms of T_f during physical aging by means of differential scanning calorimetry (DSC), we find that accessing low energy states well below T_g is triggered by a fast mechanism of equilibrium recovery, widely characterized in recent years [12,59,60]. This allows massive decrease of T_f down to the ideal glass. In this state, we find that the boson peak is essentially suppressed.

We selected PtBS as a model material because its vitrification kinetics and molecular mobility were previously deeply characterized [32,61,62]. Furthermore, PtBS, as a result of its lack of tacticity, does not crystallize under any condition as discussed in detail in the Supplemental Material [40], which includes Ref. [63]. PtBS spheres were obtained by flash precipitation [64]. Their enthalpic state and VDOS were characterized by DSC and INS. Experimental details on the production of spheres and their AFM characterization, and on DSC and INS are presented in Supplemental Material [40].

The evolution of the PtBS thermodynamic state during aging in the glassy state is presented in Fig. 2, which shows specific heat scans for the spheres at different aging times at 253 K as a showcase. A similar behavior was found for the other aging temperatures [40]. Physical aging results in the development of a pronounced endothermic overshoot, increasing in magnitude with aging time, whose onset is located ≈ 100 K below T_g and with breadth encompassing a wide range of temperatures up to T_g . This feature is well documented in glasses of different nature aged substantially below T_g [12,60,65–71], and is explained taking into account a fast mechanism of equilibrium recovery with relatively low activation energy and a time scale much smaller than that of the main α relaxation [59,72]. These results point toward the universality of a fast evolution to a relative minimum in the free energy, theoretically identified with the concept of marginal glass [73]. Other theoretical approaches also based on general features of the heterogeneity of glasses [74,75] or polymer specific

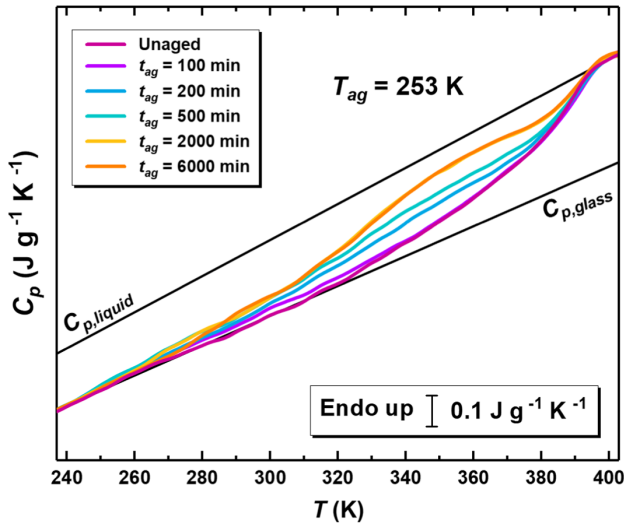


FIG. 2. Specific heat versus temperature measured by DSC upon heating at 10 K min^{-1} for spheres of PtBS aged at 253 K for different times.

approaches [76] also allow describing the nature of the fast mechanism of equilibrium recovery.

Specific heat scans on samples aged at different temperatures and aging times allow us to determine the aging time evolution of the glass enthalpic state in terms of T_f , as shown in Fig. 3. The first important feature of this plot is that, at the beginning of the aging process after cooling at 10 K/min , PtBS spheres exhibit drastic reduction in T_f ($\approx T_g$) with respect to bulk PtBS. Importantly such

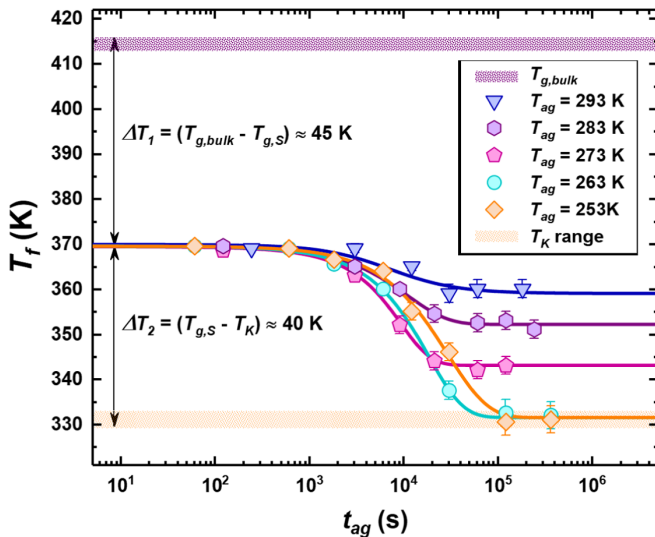


FIG. 3. Evolution of T_f as a function of aging time at the indicated aging temperatures. The upper purple hatched area indicates bulk PtBS T_g and the lower orange hatched area the temperature range below which no further T_f decrease is allowed, which is therefore identified with T_K . The solid lines are guides for the eye to highlight the long term aging plateau reached at each aging temperature.

reduction does not originate from a change in the equilibrium molecular mobility that exhibits bulk behavior (see Supplemental Material [40], which includes Ref. [77]), in line with previous results on polymer spheres [32,78]. This result indicates that vitrification on cooling is delayed to lower temperatures in spheres thanks to their ability to maintain equilibrium more efficiently than the bulk. This ability is also highlighted by the massive T_f decrease to a plateau in time scales of days. Lowering the aging temperature from 293 to 263 K results in a systematic decrease of the plateau value of T_f . In contrast, once the aging temperature is decreased below 263 K, the T_f at the long aging time plateau remains constant.

Importantly, the T_f attained upon aging at $T \leq 263 \text{ K}$ conditions is $\approx 330 \text{ K}$, which is largely below that of bulk unaged PtBS ($T_f \approx 415 \text{ K}$). This reduction would be unattainable by aging in conventional bulk glasses on experimentally accessible time scales. Furthermore, though the T_K of PtBS is unknown, the invariance of T_f at the plateau after aging at $T \leq 263 \text{ K}$ implies that no further decrease is allowed and, therefore, this T_f corresponds to T_K . Even if an indirect determination T_K of PtBS is missing, it is worth remarking that the distance from T_g is about 85 K, which is of the same order of that of polystyrene (PS), about 90 K [12], for which the T_K is well defined [79]. Hence the ideal glass is reached after mild aging at $T \leq 263 \text{ K}$, as clearly evidenced in the energetic plot presented in Fig. 4 in terms of the excess enthalpy with respect to the lowest enthalpy state with $T_f = 330 \text{ K}$ (left axis), or equivalently the fictive temperature (right axis).

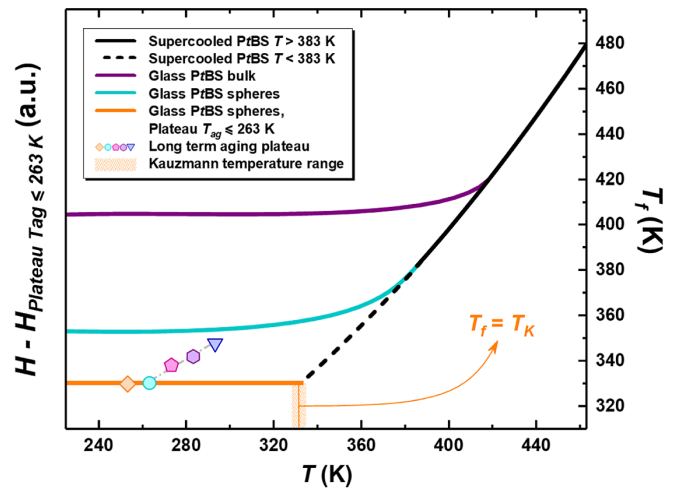


FIG. 4. Enthalpy in excess to that corresponding to $T_f = 330 \text{ K}$ (left axis) and fictive temperature (right axis) as a function of temperature for bulk PtBS and PtBS spheres in different conditions. Points are for the long term aging plateau of PtBS spheres. Lines are obtained from the temperature dependence of the specific heat on cooling at 10 K/min bulk PtBS (violet) and spheres (cyan); and both systems in the melt state (black line). The dashed black line is the extrapolation to low temperatures of the experimental melt line.

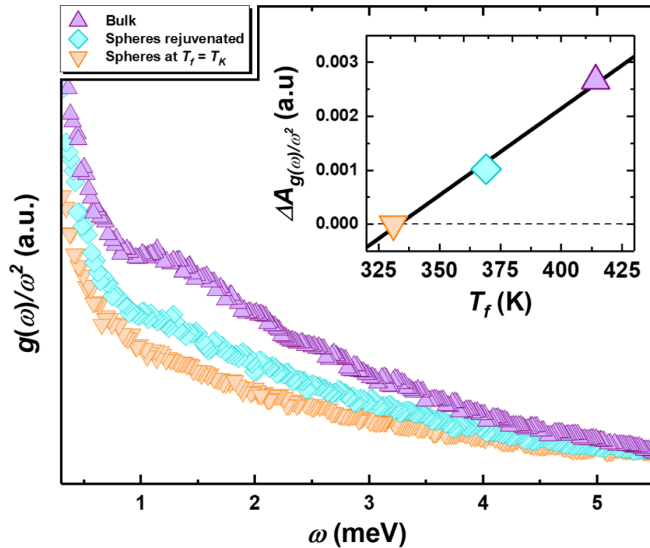


FIG. 5. Reduced VDOS for bulk PtBS, and spheres rejuvenated and aged to $T_f \approx T_K$. The inset shows the area underlying between each sample and that of PtBS spheres with $T_f \approx T_K$ as a function of the fictive temperature.

This shows that PtBS spheres aged to a plateau exhibit a kink in the enthalpy and T_f . This can be interpreted as underlying the transformation from a standard to an ideal glass and is in line with the assertion that $T_f \approx T_K = 330$ K.

The macroscopic thermodynamic overview on PtBS spheres aged deep in the glassy state is complemented by insights of extraordinary importance on the VDOS obtained by INS. Figure 5 represents the reduced VDOS, $g(\omega)/\omega^2$ —excluding the elastic peak mainly visible at low frequencies—obtained from the intermediate scattering function, $S(q, \omega)$, measured at 50 K [40]. The latter is directly measured by INS. Bulk PtBS measured immediately after cooling with 10 K/min shows the typical excess VDOS evidenced by the boson peak anomaly at $1 \div 1.5$ meV. This is significantly depleted in rejuvenated PtBS spheres, that is, taken above T_g and immediately cooled to 50 K. The boson peak is essentially suppressed after aging the spheres at 253 K for $t_{ag} \approx 10^5$ s, which is sufficient to achieve the lowest $T_f = 330$ K, identified with T_K . The inset of Fig. 5 establishes the connection between the VDOS and the thermodynamic state of the glass. It illustrates that the variation of the area below the reduced VDOS of both bulk PtBS and rejuvenated spheres in excess with respect to that of spheres aged to $T_f = 330$ K scales in a linear fashion with the glass thermodynamic state in terms of T_f .

While other studies showed that thermodynamic states corresponding to the ideal glass can be attained [12], the suppression of the boson peak observed experimentally in the ideal glass is unprecedented. This result is in line with the finding that the magnitude of the boson peak scales with the degree of disorder in the glass, i.e., the configurational

entropy, which is directly connected to T_f [33]. Hence, the boson peak progressively decreases from hyperquenched glasses [80] to hyperaged [21,37], vapor deposited [38,39] and pressure densified [81] glasses, passing from weakly aged systems [33,82,83] and eventually disappears in the ideal glass of the present study. The connection between VDOS and T_f shown in the inset of Fig. 5 proves that the microscopic vibrational properties are intimately linked to the macroscopic thermodynamic state of the glass in terms of its degree of disorder, that is, its configurational entropy [33].

The presence of large free interface is a key parameter to obtain the ideal glass, exhibiting suppression of the boson peak. Hence, our results can be discussed in light of the activity pursued on the characterization of the VDOS of glasses subjected to geometrical confinement [84]. Specifically, it is worth mentioning those works on polymer glasses subjected to “soft confinement,” where large free interface is present. Studies by inelastic neutron scattering on molecular glass former propylene glycol nanodroplets with diameter as low as ~ 4 nm suspended in decalin show disappearance of the boson peak [85]. A similar outcome was found in polymer thin films with a free interface, showing significant depression of the VDOS with respect to the bulk [86]. These studies, however, do not provide a characterization of the thermodynamic state attained in these kinds of confinement. We insinuate that the suppression of the boson peak and its relation to the corresponding energy state is a universal feature of all glasses exhibiting large amount of free interface. Hence, new impetus in the search of the ideal glass is expected in glasses of different nature, provided that their free interfacial area is magnified.

In conclusion, we have shown that increasing glasses’ free interface induces a tremendous reduction of the time scale to recover equilibrium. In appropriate conditions via a relaxation process with finite time scale deep in the glassy state, this acceleration allows attaining glass energies relevant to detect a kink in the enthalpy, identified with the transformation from the standard into the ideal glass. Concomitantly, we have shown for the first time that the boson peak disappears from the low frequency VDOS in the ideal glassy state, thus proving what has been usually conjectured.

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