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1. Introduction

The dynamics of glassy matter exhibits some common phenomena, which can be considered as hallmark features of glassy behavior, namely stretching, non-Arrhenius behavior, and ergodicity breaking [1]. 'Stretching' denotes the non-exponential relaxational response of glassy matter to external perturbations, which nowadays is commonly ascribed to heterogeneity leading to a distribution of relaxation times. Non-Arrhenius behavior shows up in the temperature dependence of dynamic quantities as, e.g., the viscosity or the relaxation time and is often assumed to mirror increasingly cooperative molecular motions when approaching the glass transition. While those phenomena usually are observed at temperatures above the glass temperature T_g, ergodicity breaking arises when the sample 'falls out of equilibrium' under cooling, which for typical cooling rates occurs close to T_g. This leaves the sample in a structural state corresponding to equilibrium at a higher temperature and leads to the observation of a variety of different, partly quite intriguing phenomena as aging, memory effects, and rejuvenation. From a theoretical viewpoint, ergodicity breaking and the resulting non-equilibrium processes are among the most challenging phenomena of glassy dynamics. They are also of considerable practical interest, e.g. for polymers, usually applied at temperatures not too far below T_g, where aging can lead to degradations of material properties. A well-known approach for the description of non-equilibrium effects in glasses is the Tool–Narayanaswamy–Moynihan (TNM) formalism [2–4]. By introducing the concepts of fictive temperature and reduced time, it takes into account the so-called non-linearity of structural relaxation during aging, caused by the fact that the relaxation time itself is time-dependent.

Aging denotes the time-dependent variation of physical quantities when a glass-forming sample reapproaches equilibrium after quenching it below T_g. This phenomenon was termed 'physical aging' by Struick [5], to distinguish it from time-dependent processes involving chemical reactions; alternative expressions used in literature are 'annealing' (if the time-dependent changes are intentional) and 'structural relaxation'. Monitoring the time-dependence of physical quantities during physical aging is a straightforward

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experiment for the investigation of non-equilibrium effects. While there are numerous recent reports on physical aging in spin glasses [6] and polymers [5,7–9], much fewer experiments were performed on canonical glass formers. Especially, having in mind that dielectric spectroscopy has proven a key technique for the study of glassy dynamics in equilibrium, it is astonishing that investigations of glassy non-equilibrium dynamics in low molecular-weight glass formers with this technique are relatively scarce [3,10–12].

Thus, in a recent work [13], we have provided detailed dielectric aging data on a variety of materials, belonging to different classes of glass formers, namely molecular glass formers and a glass-forming ionic melt, having different fragilities [1,14,15], bonding types, and being characterized by an excess wing [16] or a well-developed Johari–Goldstein β-relaxation [17]. In that work, we have introduced a new type of modeling of the experimental data by using a self-consistent recursive formula describing the time-dependence of physical properties of the glass. Using this approach we could demonstrate that the aging dynamics in all these materials is fully determined by the relaxation time and stretching parameter of the α-relaxation. In the present work, we provide further evidence for the validity of this approach by applying it to further dielectric aging data and by comparing it with an evaluation using a conventional stretched exponential ansatz. In addition, we check the data for the scaling properties, predicted on the basis of the new approach.

2. Experimental procedures

For the measurements, parallel plane capacitors having an empty capacitance up to 100 pF were used. High-precision measurements of the complex dielectric permittivity in the frequency range $10^{-4} \leqslant \nu \leqslant 10^{6}$ Hz were performed using a frequency response analyzer. At selected temperatures and aging times, additional frequency sweeps at 20 Hz $\leqslant \nu \leqslant 10^{6}$ Hz were performed with an autobalance bridge [18]. To keep the samples at a fixed temperature for up to five weeks, a closed-cycle refrigerator system was used. The samples were cooled from a temperature at least 20 K above T_g with the maximum possible cooling rate of about 3 K/min. The final temperature was reached without any temperature undershoot. As zero point of the aging times t_{age}, we took the time when the desired temperature was reached, typically about 100 s after passing T_g. The temperature was kept stable better than 0.1 K for all aging measurements.

3. Results

Fig. 1 shows the time dependence of the dielectric loss ε'' of four molecular glass formers, namely propylene carbonate (PC, $T_g \approx 159$ K, $m = 104$), propylene glycol (PG, $T_g \approx 168$ K, $m = 52$), glycerol $T_g \approx 185$ K, $m = 53$), and Salol ($T_g \approx 218$ K, $m = 73$), after quenching them to a temperature several K below T_g. Here m, taken from [15], denotes the so-called fragility index [19] giving a measure of the departure of the temperature-dependent relaxation time from Arrhenius-behavior (the lower limit of the fragility parameter is $m \approx 16$, the most fragile materials have $m \lesssim 200$). As revealed by Fig. 1, ε'' of all materials continuously decreases during aging. For long aging times t_{age}, the loss of PC and glycerol, which have been aged up to five weeks, finally becomes constant and for PG and Salol it at least shows the tendency to saturate. This indicates that the thermodynamic equilibrium state is reached after about 10^6 s. The lines are fits with a stretched exponential law as described in detail in Section 4.

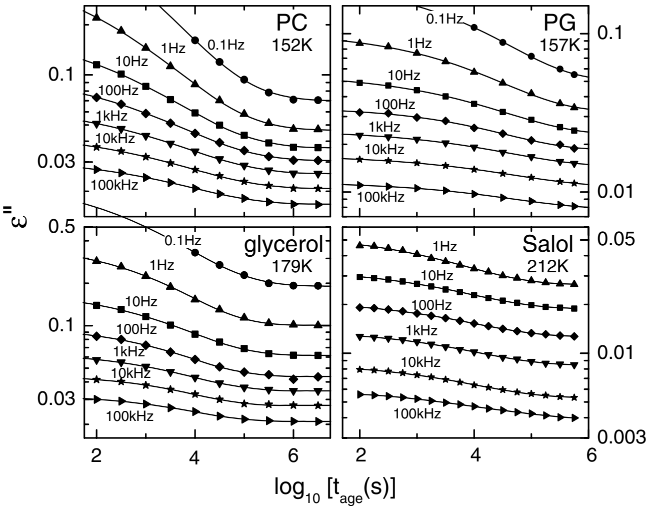

Fig. 1. Aging-time dependence of the dielectric loss of four different glass formers for various frequencies (the data on PC, PG, and glycerol were taken from [13]). The lines are fits with KWW behavior, Eq. (1), assuming a time-independent relaxation time. The errors are of similar magnitude as the width of the symbols.

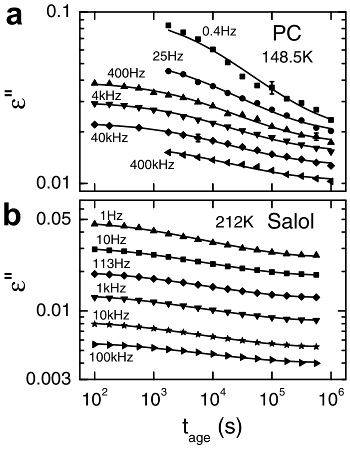

Fig. 2. Aging-time dependence of the dielectric loss of PC and Salol for various frequencies, fitted with the new approach, Eqs. (1) and (2), i.e. assuming a time dependence of the relaxation time during aging [13]. The curves at different frequencies were fitted with identical parameters ν_{st}, ν_{eq}, and β_{age}. The values of β_{age} were fixed to $\beta_{age} = 0.6$ (PC [16,26]) and 0.4 (Salol [27]). For PC, in addition the equilibrium relaxation time was fixed to $\tau_{eq} = 1.6 \times 10^{8}$ s.

In Fig. 2(a), we present aging data for PC collected at an additional lower temperature. These data and those on Salol at 212 K [Fig. 2(b)] are fitted with the modified KWW law, introduced in [13] as described in Section 4.

4. Discussion

The solid lines in Fig. 1 [20,21] show fits of these aging data using the time-honored Kohlrausch–Williams–Watts (KWW) law, routinely applied to describe *equilibrium* relaxation processes in supercooled liquids [1]:

$$\varepsilon''(t_{\mathrm{age}}) = (\varepsilon''_{\mathrm{st}} - \varepsilon''_{\mathrm{eq}}) \exp[-(t_{\mathrm{age}}/\tau_{\mathrm{age}})^{\beta_{\mathrm{age}}}] + \varepsilon''_{\mathrm{eq}} \tag{1}$$

Here the indices ‘st’ and ‘eq’ indicate the values for $t_{\mathrm{age}} \to 0$ and ∞, respectively (both being fitting parameters), τ_{age} represents the relaxation time and β_{age} the stretching parameter [12,22]. Fits and experimental data match perfectly using this ansatz (Fig. 1). However, one should be aware that it does not take into account the fact that τ_{age} should vary during aging [2–4].

As shown in Fig. 3 the resulting fit parameters τ_{age} and β_{age} exhibit considerable frequency dependence. Such a behavior was also found in the dielectric study of aging in glycerol by Leheny and Nagel [12]. A frequency-dependence of these parameters may be rationalized only if for different frequencies, different dynamic processes prevail. For example, data collected at the high-frequency flank of the α-peak should be affected by aging via the shifting of the α-peak to lower frequencies and thus show identical time dependence. In the present cases, by taking into account the equilibrium spectra obtained close to T_g [16,23,24], it can be deduced that at the lowest frequencies indeed the aging of the high-frequency flank of the α-process is detected while at the higher frequencies the excess wing or the corresponding secondary relaxation process [16,23] governs the response. Thus one could explain the observed frequency dependence in Fig. 3 by assuming that the α-relaxation and the secondary relaxation may be governed by different aging dynamics.

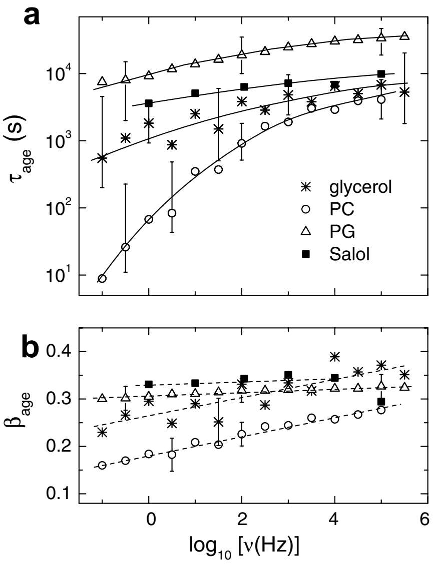

Fig. 3. Parameters of the fits with Eq. (1) to $\varepsilon''(t_{\mathrm{age}})$ shown in Fig. 1. Obviously, when assuming a time-independent relaxation time, frequency dependent parameters arise.

However, there is another problem with the results of Fig. 3: Neither the resulting τ_{age} nor β_{age} agree with the corresponding parameters τ_α and β_α, determined from an extrapolation of the equilibrium values obtained at $T > T_g$. Especially, fits with Eq. (1) yield β_{age} always much smaller than the equilibrium value [12,25]. At first glance, this seems difficult to understand as it is reasonable that the variation of ε'' during aging can be traced back to structural rearrangements and thus should be governed by the same dynamics (i.e., relaxation time) and heterogeneity (i.e., stretching parameter) as the α-relaxation. For the materials of Fig. 1, the extrapolated β_α are 0.6 (PC) [26], 0.58 (PG) [24], 0.55 (glycerol) [26], and 0.4 (Salol) [27]. These values all are significantly larger than the fit results from Eq. (1), shown in Fig. 3(b) and it is not possible to fit the data of Fig. 1 with β_{age} fixed to the extrapolated value [28]. Similar discrepancies also show up if comparing the extrapolated τ_a values with those shown in Fig. 3(a) [13].

These discrepancies are the manifestation of the so-called non-linearity of sub-T_g relaxation, a phenomenon addressed already in the works by Tool and Narayanaswamy [2]. Namely it was pointed out that during aging, τ_{age} itself is time dependent. In the Tool–Narayanaswamy–Moynihan (TNM) formalism [2–4] this is taken into account by tracing back the aging-induced variation of physical quantities to the time-dependence of the so-called fictive temperature T_f and by introducing an additional non-linearity parameter. This formalism (and other, mathematically nearly equivalent ones [11,29]) has been successfully used to describe various aging experiments (see, e.g., [4]). However, its application is not straightforward and requires some assumptions, e.g., concerning the dependence of the relaxation time and the measured quantity on T_f. As an alternative, in [13] we have proposed a new approach, that is, much simpler to apply. Considering that the α-peak frequency ν_p is a good estimate of the relaxation rate $\nu_\alpha = 1/(2\pi\tau_\alpha)$, the fact that during aging the α-relaxation peak shifts to lower frequencies [13] reflects the decrease of the relaxation rate due to the gradual drop of T_f towards the actual temperature. Thus, obviously the relaxation rate itself is subjected to aging. To take into account this time dependence, we make an ansatz for $\nu_\alpha(t_{\mathrm{age}})$, analogous to Eq. (1), namely:

$$\begin{aligned}\nu_\alpha(t_{\mathrm{age}}) &= 1/(2\pi\tau_\alpha)\\ &= (\nu_{\mathrm{st}} - \nu_{\mathrm{eq}}) \exp[-(t_{\mathrm{age}} 2\pi\nu_\alpha)^{\beta_\alpha}] + \nu_{\mathrm{eq}}\end{aligned} \tag{2}$$

One should note here that the time scale determining the aging of the relaxation rate is given by the inverse relaxation rate (i.e. the relaxation time) itself. This ansatz implies that the stretching (quantified by β_α) remains unaffected by aging, i.e., that time-temperature superposition is valid (this was evidenced, e.g., for a polymeric system in [9]). As the shift of T_f during aging is only few K for these experiments, this assumption is justified.

Eq. (2) can be easily solved numerically by recursion [30], resulting in an age dependence of τ_α that takes into account the non-linearity effects discussed above. Assuming that $\tau_{age} = \tau_\alpha$ and $\beta_{age} = \beta_\alpha$, the obtained $\tau_{age}(t_{age})$ is put into Eq. (1), which then is used to fit the measured $\varepsilon''(t_{age})$. In [13] we have demonstrated that the aging data obtained on five different glass formers, including PC, PG, and glycerol could be well described using this approach. The parameters were kept identical for all frequencies and β_{age} was fixed to the extrapolated equilibrium value. The resulting τ_{eq} values well match the extrapolated equilibrium $\tau_\alpha(T)$ curves.

In Fig. 2, we give further evidence for the applicability of the modified KWW ansatz by applying it to aging data on Salol and PC, the latter having been measured at a lower temperature than the data presented in [13]. The lines in Fig. 2 demonstrate the very good fits that are possible using this ansatz. We want to emphasize that the fits were performed simultaneously for *all* curves, with the parameters of Eq. (2) identical for *all* frequencies. The curves for different frequencies are only distinguished by the parameters ε''_{st} and ε''_{eq}. The number of fit parameters for each curve is four (β being fixed to the extrapolated equilibrium value), however, two of them being common for all curves. Thus much less parameters are involved, compared to the conventional KWW fits of Fig. 1. For each material, the obtained $\varepsilon''_{st}(\nu)$ curve (not shown) nearly matches the $\varepsilon''_{st}(T)$ curve measured at T_g, thus indicating that at the beginning of the aging $T_f \approx T_g$. From the fits, we obtain an average relaxation time $\langle\tau_{eq}\rangle = 3.7 \times 10^4$ s for Salol, which well matches the published $\langle\tau\rangle(T)$ behavior of Salol [27,31], extrapolated to 212 K. For PC at 148.5 K [Fig. 2(a)] the problem arises that this temperature is too far below T_g to come close to thermodynamic equilibrium within reasonable times, especially as this is a rather fragile glass former with a very steep $\tau(T)$ curve close to the glass transition. Thus from the fits shown in Fig. 2, it is not possible to gather reliable information on the equilibrium relaxation time. Therefore, ν_{eq} was fixed to a value of 1×10^{-9} Hz, corresponding to $\langle\tau_{eq}\rangle = 2.4 \times 10^8$ s, consistent with an extrapolation of $\tau(T)$ of PC [26,32]. Thus, also for this lower temperature, in PC the aging results can be described in full accord with the equilibrium results on the α-relaxation, using the new approach proposed in [13].

As already noted in [13], it is remarkable that, independent of the spectral region (α-peak, excess wing, or β-peak), the aging dynamics of ε'' is always dominated by the structural α-process. It is the structural rearrangement during aging, which in a direct way (by shifting the α-peak to lower ν) influences $\varepsilon''(t_{age})$ in the α-peak region and in a more indirect way (by varying the structural 'environment' felt by the relaxing entities) in the other regions. It should be noted that, while in the present work only data have been analyzed that reflect the aging at frequencies above the α-peak frequency, also data at the low-frequency wing of the α-peak, showing an *increase* of $\varepsilon''(t_{age})$ with time can be taken into account by Eqs. (1) and (2). This is done by using $\varepsilon''_{eq} > \varepsilon''_{st}$ in Eq. (1) and was demonstrated for the ionic-melt glass former $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN) in [13]. However, if during aging a transition between different spectral regimes occurs, e.g., from the low- to the high-frequency flank of the α-peak leading to a maximum in $\varepsilon''(t_{age})$, the simple description with Eqs. (1) and (2) must fail.

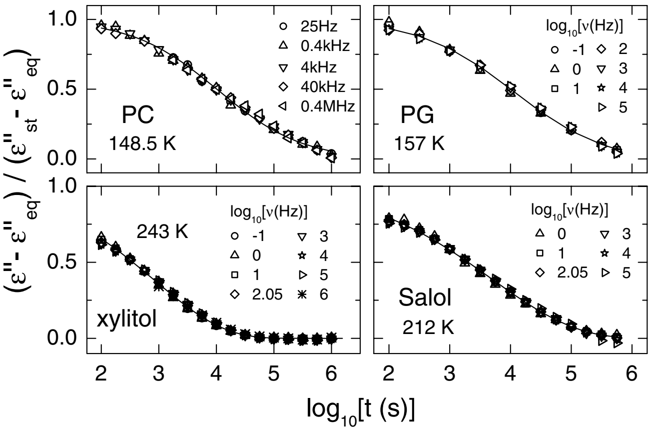

Fig. 4. Scaling of the aging curves for different frequencies for four glass formers. The values of ε''_{st} and ε''_{eq} were obtained from the fits with the modified KWW approach, shown in Fig. 2 (PC and Salol) and in [13] (PG and xylitol). For PC the data set at 0.4 Hz was omitted as it shows rather strong scattering [cf. Fig. 2(a)]. The lines correspond to the fitting curves.

The fact that the fits for different frequencies in Fig. 2 only differ by the values of ε''_{st} and ε''_{eq} implies that it should be possible to scale the $\varepsilon''(t_{age})$ curves for different frequencies onto one master curve by plotting the quantity $(\varepsilon'' - \varepsilon''_{eq})/(\varepsilon''_{st} - \varepsilon''_{eq})$ versus the aging time. In [13] a nearly perfect scaling was reported for glycerol. In Fig. 4 we provide the scaling plots for two of the glass formers analyzed in [13] and for the new data on PC and Salol of the present work. In all cases the scaling works reasonably well. The lines show the fit curves, which naturally collapse onto one line in the scaling plots. For PC the scaling is least perfect and for this material the scaling plot also reveals systematic deviations of fit and experimental data at the longest aging times. Probably this is due to the fact that for this rather low temperature, the sample is still far from equilibrium and the fixed value of τ_{eq} should be chosen even larger. However, it is also possible that for larger temperature jumps limitations of the introduced modified KWW approach show up. In this context it is interesting that in [12], for temperatures far below T_g, deviations from the TNM model were reported.

5. Conclusions

In conclusion, the analysis of aging data on a number of different glass formers using a conventional KWW ansatz, performed in the present work, has revealed marked deviations of the resulting relaxation parameters from those obtained from equilibrium data. In contrast, the alternative approach proposed in [13], which takes into account the time dependence of the relaxation time, successfully describes results at different frequencies with identical relaxation time and stretching parameter, both being fully consistent with equilibrium data. In the present work, this approach was successfully applied to time-dependent data on Salol and PC, giving further evidence for its applicability for the description of aging data. Our results also corroborate the conclusion drawn in [13] that all dynamic processes age in a similar way, determined by the structural α-relaxation dynamics.

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