

## Glassy Aging Dynamics

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We present time-dependent dielectric loss data for various glass formers below the glass temperature. The observed aging dynamics is described using a modified Kohlrausch-Williams-Watts law taking into account the variation of the relaxation time during aging. It leads to values for the aging relaxation time and stretching exponent, fully consistent with the results from equilibrium measurements performed at higher temperatures. Irrespective of the dynamic process prevailing in the investigated frequency region, the aging dynamics is always determined by the structural relaxation process.

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One of the hallmark features of glassy dynamics is the so-called “ergodicity breaking” [1], occurring not only in canonical glasses, but also, e.g., in spin glasses [2]. It arises when the sample is cooled too fast for the molecules to arrange into an equilibrated state; i.e., the sample “falls out of thermodynamic equilibrium.” For typical cooling rates, this occurs close to the glass temperature  $T_g$  and leaves the sample in a structural state corresponding to a higher temperature. Then a variety of intriguing phenomena as aging, memory effects, and rejuvenation are observed. From a theoretical viewpoint, nonequilibrium processes are among the most challenging phenomena of glassy dynamics. They are also of considerable practical interest for the degradation of glassy material properties, e.g., of polymers. A straightforward experiment for the investigation of nonequilibrium effects is to monitor the time-dependent variation of physical quantities after quenching the sample below  $T_g$ . Then the so-called “physical aging” [3] takes place; i.e., the physical quantities vary with time when the sample reapproaches equilibrium. While there are numerous recent reports on physical aging in spin glasses [2] and polymers [3–6], much fewer experiments were performed on canonical glass formers so far, and especially investigations of nonequilibrium dynamics with dielectric spectroscopy are relatively scarce [5–10]. In this Letter, we provide detailed dielectric aging data on a variety of materials belonging to different classes of glass formers. By introducing a new type of modeling of the experimental data, we demonstrate that the aging dynamics in all these materials is fully determined by the relaxation time and stretching parameter of the  $\alpha$  relaxation.

The dielectric aging experiments were performed as described in [11]. During the aging time of up to nine weeks, the temperature was kept stable better than 0.1 K. Figure 1(a) shows the time dependence of the dielectric loss  $\varepsilon''$  of glycerol at a frequency  $\nu = 10$  Hz. Glycerol, being a hydrogen-bonded network glass former with  $T_g \approx 185$  K and intermediate fragility  $m \approx 53$  [1,12–14], belongs to the most investigated glass formers. During aging, its loss decreases continuously with  $t_{\text{age}}$  and finally becomes constant, indicating that the thermodynamic equi-

librium state is reached after about  $10^6$  s. To fit such a kind of data, it seems natural to employ the time-honored Kohlrausch-Williams-Watts (KWW) law, routinely used to describe *equilibrium* relaxation processes in supercooled liquids [1]. Indeed, a perfect fit [solid line in Fig. 1(a)] is achieved using the ansatz

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

where the indices “st” and “eq” indicate the values for  $t_{\text{age}} \rightarrow 0$  and  $\infty$ , respectively (both being fitting parameters),  $\tau_{\text{age}}$  is the relaxation time, and  $\beta_{\text{age}}$  is the stretching parameter [10,15]. However, as already revealed in the seminal study by Leheny and Nagel [10], neither  $\tau_{\text{age}}$  nor  $\beta_{\text{age}}$  agree with the corresponding parameters  $\tau_{\alpha}$  and  $\beta_{\alpha}$ ,

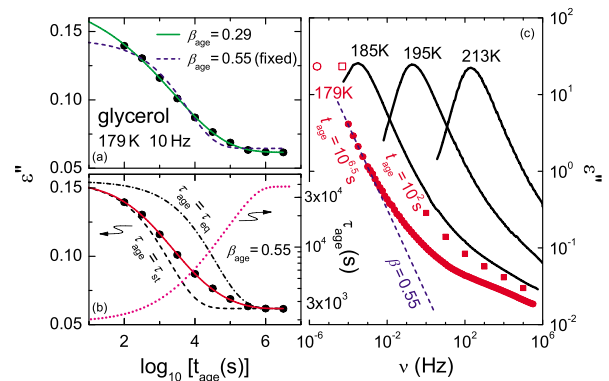


FIG. 1 (color online). (a)  $\varepsilon''(t_{\text{age}})$  of glycerol. Lines: Analysis with Eq. (1) with all parameters free (solid line) or with  $\beta_{\text{age}}$  fixed at 0.55 (dashed line). (b) Left scale: Same data fitted with the modified KWW ansatz with  $\tau_{\text{age}}(t_{\text{age}})$  determined from Eq. (2) and  $\beta_{\text{age}} = 0.55$  (solid line). The dashed and dash-dotted lines were calculated from Eq. (1) with  $\tau_{\text{age}} = \tau_{\text{st}}$  and  $\tau_{\text{age}} = \tau_{\text{eq}}$ , respectively. Right scale:  $\tau_{\text{age}}(t_{\text{age}})$  as obtained from Eq. (2) (dotted line). (c) Loss spectra for the shortest and longest  $t_{\text{age}}$  (closed symbols), together with equilibrium data (solid lines) at higher temperatures [11,18]. The dashed line demonstrates a slope of 0.55. The open symbols indicate the peak frequencies for  $t_{\text{age}} \rightarrow 0$  (squares) and  $\infty$  (circles), calculated from the parameters of the fit shown in (b).

determined from an extrapolation of fit results of the equilibrium spectra at  $T > T_g$ , and, in addition, they exhibit a considerable frequency dependence [16]. Especially, fits with Eq. (1) yield  $\beta_{\text{age}}$  always much smaller than the equilibrium value [10,16,17]. In the present case the extrapolated  $\beta_\alpha$  is 0.55 [18], significantly larger than  $\beta_{\text{age}} = 0.29$ , and it is not possible to fit the data with  $\beta_{\text{age}}$  fixed to 0.55 (dashed line). At first glance, this seems difficult to understand as it is reasonable that the variation of  $\varepsilon''$  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  $\alpha$  relaxation. This discrepancy is the manifestation of the nonlinearity of sub- $T_g$  relaxation, a phenomenon addressed already in the famous works by Tool and Narayanaswamy [19]. Namely, it was pointed out that during aging,  $\tau_{\text{age}}$  itself is time dependent. In the Tool-Narayanaswamy-Moynihan (TNM) formalism [7,19,20] 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 nonlinearity parameter. This formalism (and other mathematically nearly equivalent ones [9,21]) has been successfully used to describe various aging experiments (see, e.g., [20]). But its application is not straightforward, and an important point of the present work is the analysis of our data using a much simpler new approach.

Figure 1(c) shows  $\varepsilon''(t_{\text{age}})$  for the shortest (100 s) and longest ( $10^{6.5}$  s) aging times, together with spectra at  $T > T_g$  [18]. Obviously, during aging the peak frequency  $\nu_p$ , which gives a good estimate of the relaxation rate  $\nu_\alpha = 1/(2\pi\tau_\alpha)$ , shifts towards lower values, which reflects the gradual drop of  $T_f$  towards the actual temperature. Thus we use an ansatz for  $\nu_\alpha(t_{\text{age}})$ , equivalent to Eq. (1):

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

This relation,  $\nu_\alpha = f(\nu_\alpha)$ , can be numerically solved by iteration [22], resulting in an age dependence of  $\tau_\alpha$  gradually increasing between the two plateau values  $\tau_{\text{st}} = 1/(2\pi\nu_{\text{st}})$  and  $\tau_{\text{eq}} = 1/(2\pi\nu_{\text{eq}})$  [23]. Assuming that  $\tau_{\text{age}} = \tau_\alpha$  and  $\beta_{\text{age}} = \beta_\alpha$ , the obtained  $\tau_{\text{age}}(t_{\text{age}})$  is put into Eq. (1), which then is used to fit the measured  $\varepsilon''(t_{\text{age}})$ . The resulting fit, with  $\beta_{\text{age}} = \beta_\alpha$  fixed to 0.55, is shown in Fig. 1(b) (left scale, solid line) together with  $\tau_{\text{age}}(t_{\text{age}})$  from Eq. (2) (right scale). The dashed and dash-dotted lines indicate conventional KWW curves using  $\beta = 0.55$  and with  $\tau = \tau_{\text{st}}$  and  $\tau = \tau_{\text{eq}}$ , respectively, as obtained from the fit. It is the transition from the first to the latter curve during aging, which leads to the apparently larger “stretching” of the  $\varepsilon''(t_{\text{age}})$  curve. This ansatz implies that the stretching remains unaffected by aging, i.e., that time-temperature superposition is valid (this was evi-

denced, e.g., for a polymeric system in [6]). As the shift of  $T_f$  during aging is only a few K for these experiments, this assumption is justified.

As shown in Fig. 2(a), this modified KWW ansatz was used to fit  $\varepsilon''(t_{\text{age}})$  of glycerol resulting in a perfect agreement. As the aging time dependence of  $\tau$  can be assumed to be independent of the frequency, the fits were performed simultaneously for all curves, with the parameters of Eq. (2) identical for all  $\nu$ . The curves for different  $\nu$  are distinguished only by the parameters  $\varepsilon_{\text{st}}$  and  $\varepsilon_{\text{eq}}$ . Thus the number of parameters for each curve is four ( $\beta$  being fixed to 0.55) with, however, two of them being common for all curves. This also implies that it should be possible to scale the  $\varepsilon''(t_{\text{age}})$  curves for different  $\nu$  onto one master curve in the way given in Fig. 2(b), which, indeed, is the case. (In contrast, a different scaling procedure proposed for spin glasses, which involves the scaling of the abscissa, too, was found not to work for glycerol [10]). Further corroboration arises from the values of the relaxation peak frequencies obtained from the fit parameters  $\nu_{\text{st}}$  and  $\nu_{\text{eq}}$ , shown as open symbols in Fig. 1(c). They are fully consistent with a low-frequency extrapolation of the two aging curves at the shortest and longest  $t_{\text{age}}$ . From Fig. 1(c), it becomes obvious that, depending on  $\nu$ , the  $\varepsilon''(t_{\text{age}})$  curves in Fig. 2 reflect aging in the region of the right flank of the  $\alpha$  peak or in the region of the so-called excess wing showing up as a

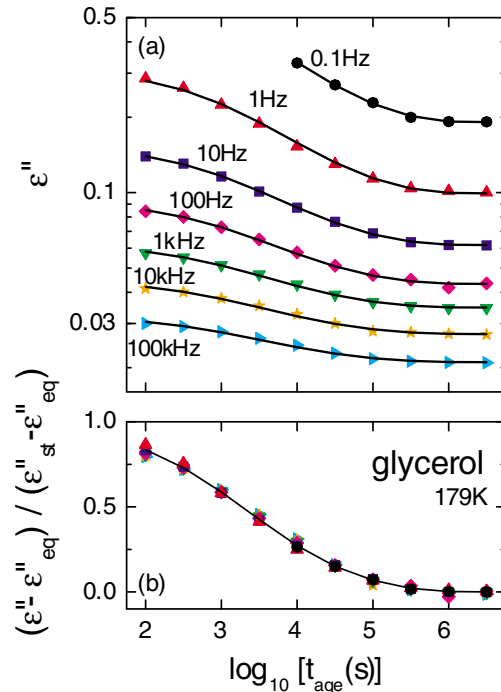


FIG. 2 (color online). (a)  $\varepsilon''(t_{\text{age}})$  of glycerol at 179 K for various frequencies. The lines are fits with the modified KWW ansatz with  $\beta_{\text{age}}$  fixed to the equilibrium value of 0.55 and identical values of  $\nu_{\text{st}}$  and  $\nu_{\text{eq}}$  for all frequencies. (b) Scaling of the curves for different frequencies, using the values of  $\varepsilon''_{\text{st}}$  and  $\varepsilon''_{\text{eq}}$  obtained from the fits shown in (a).

second power law at high frequencies [11,24]. Recent experiments have demonstrated that the excess wing is caused by a separate relaxation process [11,25,26]. Thus, independently of the dynamic process prevailing, the aging dynamics of  $\epsilon''$  is always dominated by the  $\alpha$  process.

In Fig. 3, we show aging data for four further glass formers. Propylene carbonate (PC,  $T_g \approx 159$  K,  $m = 104$  [13]), propylene glycol (PG,  $T_g \approx 168$  K,  $m = 52$  [13]), and xylitol ( $T_g \approx 248$  K,  $m = 94$  [26,27]) are molecular glass formers. PC is a van der Waals liquid, while for PG and xylitol a hydrogen-bonded network can be assumed. While the equilibrium spectra of PC and PG exhibit an excess wing [11,24], xylitol [26,27] reveals a well pronounced Johari-Goldstein (JG)  $\beta$ -relaxation peak [28]. Finally,  $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$  (CKN,  $T_g \approx 333$  K,  $m = 93$ ) is a typical ionic-melt glass former. For xylitol [Fig. 3(c)], remarkably the curve at 1 kHz crosses the one at 10 Hz. This can be ascribed to the low-frequency results reflecting the aging of the  $\alpha$  process, while at higher  $\nu$  the aging in the regime of the JG  $\beta$  process is observed [22,26,27]. For CKN [Fig. 3(d)], where the dielectric response is dominated by charge transport instead of dipolar reorientations, we plot the imaginary part of the dielectric modulus  $M''$ . In ionically conducting glass formers as CKN, this is common practice, because  $M''$  usually reflects the structural relaxation behavior and because conductivity contributions, dominating  $\epsilon''(\nu)$  at low frequencies, are suppressed [29,30]. As the relaxation peaks showing up in  $M''(\nu)$  are known to be located at higher frequencies than those in  $\epsilon''(\nu)$ , also aging data at the low-frequency flank of the  $\alpha$  peak, *increasing* with time, could be collected [curve at 1 Hz in Fig. 3(d)].

For all these cases, good fits could be achieved using Eqs. (1) and (2), the only exception being  $M''(t_{\text{age}})$  of CKN

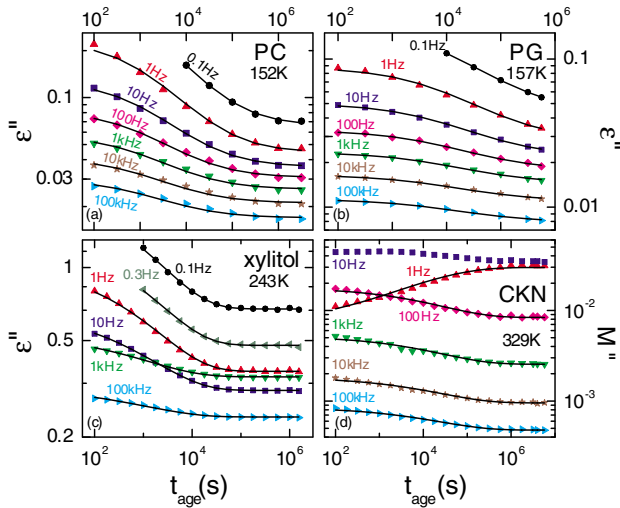


FIG. 3 (color online). (a)–(c)  $\epsilon''(t_{\text{age}})$  and (d)  $M''(t_{\text{age}})$  of four different glass formers for various frequencies. The lines are fits as described in Fig. 2(a) with  $\beta_{\text{age}} = 0.6$  (PC [11,18]), 0.58 (PG [22,25]), 0.43 (xylitol [22]), and 0.4 (CKN, from structural relaxation [30]).

at 10 Hz, exhibiting a shallow maximum. As for glycerol (Fig. 2), the parameters of Eq. (1) were kept identical for all frequencies, and  $\beta_{\text{age}}$  was fixed to the equilibrium value. In addition, for PC also aging data collected at a second temperature ( $T = 148.5$  K, not shown) could be successfully described in this way [22]. (To check the validity of this formalism at temperatures even further below  $T_g$ , where deviations from the TNM model were reported [10], experiments with aging times in the order of years are required [22].) The resulting values of  $\tau_{\text{eq}}$  are shown in Fig. 4 (closed symbols). They perfectly match the equilibrium  $\tau_{\alpha}(T)$  curves at  $T > T_g$  [11,18,22,25,30]. For ionically conducting glass formers as CKN, decoupling phenomena are known to arise at low  $T$ . They lead to deviations of the dielectric  $\alpha$ -relaxation times  $\tau_{\text{die}}^{\text{el}}$ , from the “true” structural  $\alpha$ -relaxation times  $\tau_{\text{struct}}$ , determined, e.g., by mechanical experiments [30]. As revealed by Fig. 4,  $\tau_{\text{eq}}$  of CKN seems not to match  $\tau_{\text{die}}^{\text{el}}(T)$  (the curve would have to bend up unreasonably strongly) but  $\tau_{\text{struct}}(T)$ , obtained from shear experiments [31]. This indicates that the aging dynamics is governed by the structural relaxation time. Thus, despite being determined by monitoring the aging of a quantity related to ionic transport (for CKN) or dipolar reorientation (for the other glass formers), the obtained  $\tau_{\text{eq}}$  is the *structural*  $\alpha$ -relaxation time. In the dipolar glass formers, it matches the equilibrium dielectric relaxation times (Fig. 4) because translational-reorientational decoupling is less important or even absent (demonstrated for glycerol in [32]).

It is an important result of this work that, independently of the spectral region ( $\alpha$  peak, excess wing, or  $\beta$  peak) and of the relaxing entities (dipoles or ionic charge carriers), the aging dynamics of  $\epsilon''$  is always dominated by the structural  $\alpha$  process. It is the structural rearrangement during aging, which in a direct way (by shifting the  $\alpha$

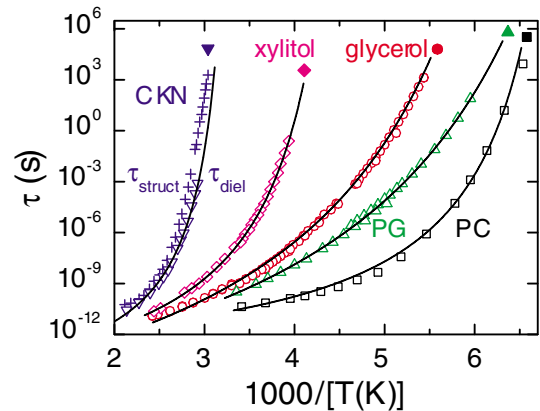


FIG. 4 (color online).  $\alpha$ -relaxation times from dielectric equilibrium measurements for the investigated glass formers (open symbols) [11,18,22,25,30]. The lines are fits with the Vogel-Fulcher-Tammann law. For CKN, in addition, the structural relaxation time from mechanical spectroscopy is plotted (pluses) [31]. The closed symbols show the equilibrium average relaxation times  $\langle\tau_{\text{eq}}\rangle$ , obtained from the fits in Figs. 2(a) and 3.

peak to lower  $\nu$ ) influences  $\varepsilon''(t_{\text{age}})$  in the  $\alpha$ -peak region and in a more indirect way (by varying the structural “environment” felt by the relaxing entities) in the other regions. Here no statement needs to be made of what way the aging may affect the other processes. For example, irrespective of the question if in the  $\beta$ -relaxation regime the aging affects the  $\beta$ -relaxation time or reduces the peak amplitude (or both) [11,28,33], the time dependence of this variation is determined by the structural  $\alpha$  relaxation. This indicates that the secondary relaxation in xylitol and those causing the excess wings in glycerol, PC, and PG are not due to localized intramolecular modes, but of intermolecular origin, i.e., true JG relaxations [28]. If during aging a transition between different regimes occurs, the simple description with Eqs. (1) and (2) must fail. This is the case for CKN at 10 Hz. Here a transition from the low- to the high-frequency flank of the  $\alpha$  peak takes place (compare the nonequilibrium spectra at 325 K in [30]), which leads to a maximum in  $M''(t_{\text{age}})$  [Fig. 3(d)].

The straightforward description of aging dynamics with Eqs. (1) and (2) successfully describes results at different frequencies with identical relaxation times and stretching parameters, both being fully consistent with equilibrium data. This ansatz works equally well also for the real part of the dielectric permittivity  $\varepsilon'$  (not shown), and it may also be used to describe other quantities. Our analysis reveals that all dynamic processes age in a similar way, determined by the structural  $\alpha$ -relaxation dynamics. Success certainly justifies this to some extent phenomenological ansatz. But one may ask, e.g., why Eq. (2) should not be applied on  $\tau_\alpha$  instead of  $\nu_\alpha$ . However, using such an ansatz does not lead to an equally consistent description; e.g.,  $\tau_{\text{eq}}$  does not match the  $\tau_\alpha(T)$  from equilibrium measurements. Obviously, it is the rate that ages with KWW, but a theoretical foundation still needs to be found.

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