Glassy aging with modified Kohlrausch-Williams-Watts form

Bhaskar Sen Gupta and Shankar P. Das

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

In this paper, we address the question of whether aging in the nonequilibrium glassy state is controlled by the equilibrium α-relaxation process, which occurs at temperatures above T_g. Recently, Lunkenheimer *et al.* [Phys. Rev. Lett. **95**, 055702 (2005)] proposed a model for the glassy aging data of dielectric relaxation using a modified Kohlrausch-Williams-Watts form $\exp[-(t_{age}/\tau_{age})^{\beta_{age}}]$. The aging time t_{age} dependence of the relaxation time τ_{age} is defined by these authors through a functional relation involving the corresponding frequency $\nu(t_{age}) = 1/(2\pi\tau_{age})$, but the stretching exponent β_{age} is the same as β_α, the α-relaxation stretching exponent. We present here an alternative functional form for $\tau_{age}(t_{age})$ directly involving the relaxation time itself. The proposed model fits the data of Lunkenheimer *et al.* perfectly with a stretching exponent β_{age} different from β_α.

Understanding the dynamics of the supercooled liquid in the nonequilibrium state has been one of the most challenging problems in condensed matter physics. When cooled fast enough, the supercooled liquid remains trapped in a specific part of the phase space of the constituent particles and cannot equilibrate. For such a system, the relaxation time to equilibrium increases far beyond the time scale of the experiment. Analysis of the dynamics of the liquid in the nonequilibrium state reveals a variety of phenomena like aging and memory effects [1,2]. Theoretical approaches for understanding the complex relaxation behavior in the nonequilibrium state include computer simulations [3] and study of simple dynamical models [4]. An important question in this regard is whether the dynamics in the nonequilibrium state can be understood as an extrapolation of the α-relaxation process characteristics of the equilibrium states at temperatures above the calorimetric glass transition temperature T_g [1]. In a recent Letter, Lunkenheimer *et al.* [5] have studied the time-dependent dielectric loss data [6] for various glass formers below the glass transition temperature. By modeling the experimental data with a modified Kohlrausch-Williams-Watts (KWW) form $\exp\{-[t_{age}/\tau_{age}(t_{age})]^{\beta_{age}}\}$, these authors demonstrate that the nonequilibrium dynamics is fully determined by the relaxation times and the stretching parameters of the equilibrium α-relaxation process at $T > T_g$. In the present report, we demonstrate that the data of Ref. [5] can also be fitted in an alternative scheme with a modified KWW form the same as that proposed in Ref. [5], but with a relaxation time τ_{age} whose time evolution is entirely different. Furthermore, the proposed model, which fits the data of Ref. [5] perfectly, obtains a stretching exponent *different* from that of the corresponding α relaxation. It therefore conforms to a scenario in which the nature of the relaxation and heterogeneity controlling the aging process is different from that of the equilibrium structural relaxation.

First we consider here the data of dielectric loss ϵ'' [5] for glycerol at 179 K (having calorimetric glass transition temperature $T_g = 185$ K and fragility $m = 53$ [7,8]) over the frequency range $1-10^5$ Hz. During aging, ϵ'' for each frequency decreases continuously with increasing t_{age}, approaching the equilibrium value over the longest time scale of 10^6 s. If the aging data are fitted with the simple

stretched exponential form, we obtain a stretching exponent β and a relaxation time τ which are very different from those corresponding to the equilibrium α relaxation at $T > T_g$ [9]. The data for the dielectric relaxation function are fitted in this case to the form

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

where the subscripts "st" and "eq" respectively refer to the initial ($t_{age} \to 0$) and the long-time ($t_{age} \to \infty$) limiting values of ϵ''. In such a scheme generally both ϵ''_{st} and ϵ''_{eq} are obtained as the best values for the corresponding fitting parameters. The relaxation time τ_{age} and stretching exponent β_{age} of the KWW form are also used as free fit parameters. The quality of this fitting with the dielectric data from different samples is available in Ref. [10] (see Figs. 1 and 2 there). Both τ_{age} and β_{age} as obtained from the fitting of the relaxation data in the aging regime show strong frequency dependence. If, on the other hand, we adopt a fitting scheme in which β_{age} is kept fixed at its corresponding α-relaxation value $\beta_\alpha = 0.55$, then the data *do not* fit the form (1) with only τ_{age} as a free fit parameter. The poorness of such a fitting procedure is discussed further below (see Fig. 4).

An interesting interpretation of these data came from Lunkenheimer *et al.* by using a modified KWW form with the relaxation time τ_{age} being dependent on aging time t_{age} [11,12]. However, in Ref. [5], the time dependence of τ_{age} is prescribed in terms not of the relaxation time but of the corresponding frequency ν_{age}, which is defined as

$$\nu(t_{age}) = \frac{1}{2\pi\tau_{age}(t_{age})}. \quad (2)$$

Lunkenheimer *et al.* choose the aging time dependence of ν in (2) in the following form:

$$\nu_{age}(t_{age}) = (\nu_{st} - \nu_{eq})\exp[-(2\pi\nu t_{age})^{\beta_\alpha}] + \nu_{eq}. \quad (3)$$

According to (3), the relaxation time $\tau_{age} \to 1/(2\pi\nu_{st})$ and $1/(2\pi\nu_{eq})$ as $t_{age} \to 0$ and ∞, respectively. Lunkenheimer *et al.* obtain almost a perfect fit for the dielectric data over the whole frequency range with the above choice of the time dependence for the relaxation time. They observe that an important feature of this aging process is that the stretching

exponent β_{age} is the *same* as that of the α relaxation, β_α. It therefore implies that the stretching of the relaxation remains unaffected by aging below T_g and hence confirms the validity of the time-temperature superposition during the aging process. Furthermore, the best-fit value obtained for ν_{eq} in (3) corresponds to a time , $\tau_{\mathrm{eq}}=1/(2\pi\nu_{\mathrm{eq}})$ which agrees with the α-relaxation time τ_α for glycerol extrapolated from higher temperatures ($T>T_g$) to sub-T_g regions. This matching of τ_{eq} with the extrapolated equilibrium α-relaxation time values in the case of glycerol will be further discussed below with Fig. 5.

While this is a very instructive way of interpreting the evolution of the nonequilibrium state, the ansatz (3) for determining the time evolution of τ_{age} in terms of the corresponding frequency is somewhat unnatural. Instead of the relaxation time itself being time dependent, the corresponding frequency ν becomes time dependent in (3). The latter is then transmitted to τ_{age} through the standard relation (2). As an alternative to this, in the present paper we adopt a more natural scheme for the time evolution of the relaxation time τ_{age} in the following manner.

$$\tau_{\mathrm{age}}(t_{\mathrm{age}}) = (\tau_{\mathrm{st}} - \tau_{\mathrm{fn}})f(t_{\mathrm{age}}) + \tau_{\mathrm{fn}}, \qquad (4)$$

where the function $f(t)$ reduces to the value 1 or 0 for $t \to 0$ or ∞, respectively, so that the relaxation time τ_{age} attains the asymptotic values τ_{st} and τ_{fn}, respectively, in the above two limits. A perfect fit is obtained for all the $\epsilon''(t_{\mathrm{age}})$ data at different frequencies using Eq. (1) with $\tau_{\mathrm{age}}(t_{\mathrm{age}})$ being determined with the ansatz (4). In doing this the choice of the function $f(t)$ is not unique. However, there are some characteristics that can be associated with this function. As indicated above, it must change from 1 to 0 as the time changes from the $t=0$ to ∞ limit. It is plausible to expect that the time dependence of $f(t)$ is changing monotonically from 1 to 0. We have tested in terms of a reduced time $x=t/\tau$, where τ is the relaxation time, the following three options: (a) exponential (simple or stretched) relaxation such as $\exp(-x^\beta)$, (b) power-law-type decays $x^{-\alpha}$, or (c) a function that decays as $\tanh(x)$. Among these the last form gives the best fit to the aging data. We obtain for the normalized function $f(t)$

$$f(t) = \frac{a_0}{(1+e^{2t/\tau(t)})^\beta}, \qquad (5)$$

where $a_0=2^{1/\beta}$ is a normalization constant to ensure that $f(t)$ reduces to the above stated values in the two limits. Note that for times large compared to the relaxation times this function also behaves like a stretched exponential function with exponent β. Therefore the function defined in the self-consistent Eq. (5) also represents stretching of the relaxation process. The exponent β for the stretching process is assumed to be same as the stretching exponent β_{age} used in the modified KWW form to keep the number of fitting parameters to a minimum. Thus, in spite of the differences in the defining relations for the respective τ's, β_{age} represents stretching of the relaxation process in both cases (Ref. [5] and ours). The fittings (corresponding to different ω's) over the whole frequency range of the dielectric data are shown in Fig. 1. In the present fitting scheme, unlike that of Ref. [5],
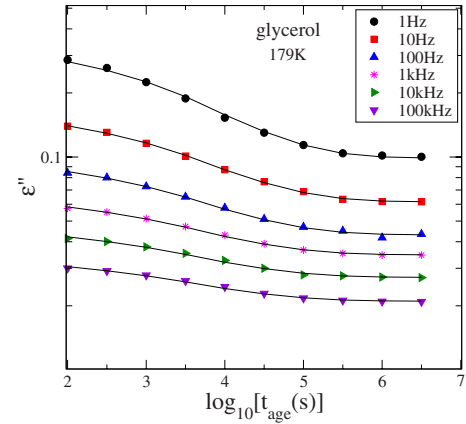

FIG. 1. (Color online) $\epsilon''(t_{\mathrm{age}})$ data for glycerol at 179 K vs t_{age} (s) at the frequencies displayed in the inset. Solid lines correspond to the best fits using the modified KWW form with $\tau_{\mathrm{age}}(t_{\mathrm{age}})$ determined from Eq. (4).

we obtain a stretching exponent $\beta_{\mathrm{age}}=0.29$ which is *different* from the corresponding α-relaxation value $\beta_\alpha=0.55$. The best-fit values for the parameters ϵ''_{st} and ϵ''_{st} (at a given frequency) obtained, respectively, in the present work and Ref. [5] agree closely. This comparison is displayed in Fig. 2, We display next in Fig. 3 the aging time dependence of τ_{age} in our calculation and that of Ref. [5]. In the present case, the relaxation time is strongly time dependent at the initial stage and saturates relatively earlier as t_{age} reaches the time τ_{fn} (say). In our fitting scheme the best-fit result value for τ_{fn} is very different from the corresponding τ_{eq} of Lunkenheimer *et al.* and cannot be simply related to the α-relaxation process. All the dielectric data for ϵ'' scale into a single master curve as shown in Fig. 4. In the same figure we display the curve corresponding to the fitting of Lunkenheimer *et al.*, which is practically indistinguishable from ours. We also display here, for comparison, the best-fitting curves which are obtained with a simple KWW function having constant relaxation
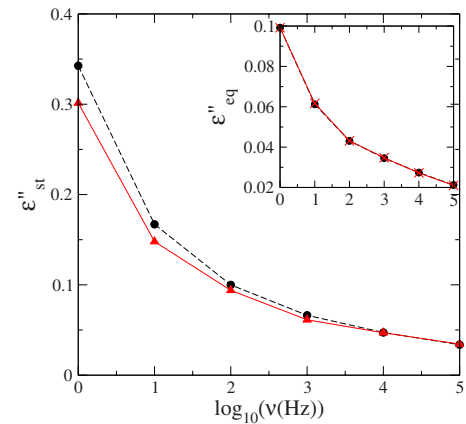

FIG. 2. (Color online) Best-fit values of ϵ''_{st} for the curves in Fig. 1 vs frequency ν (Hz) as obtained with the present work (solid line) and the corresponding results of Ref. [5] (dashed). The inset shows the best-fit ϵ''_{eq} with frequency ν respectively from the present work and Ref. [5].
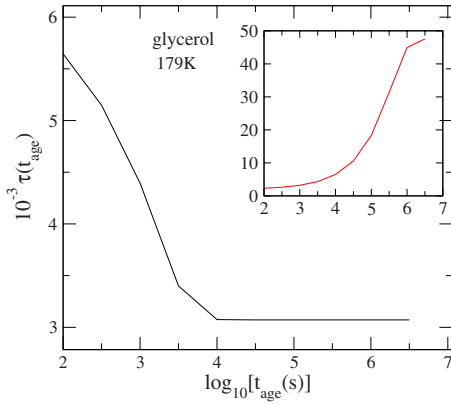
FIG. 3. (Color online) Best-fit $\tau(t_{age})$ vs t_{age} (s) for glycerol using ansatz (4) of the present work. Result of Ref. [5] for $\tau(t_{age})$ as inset.
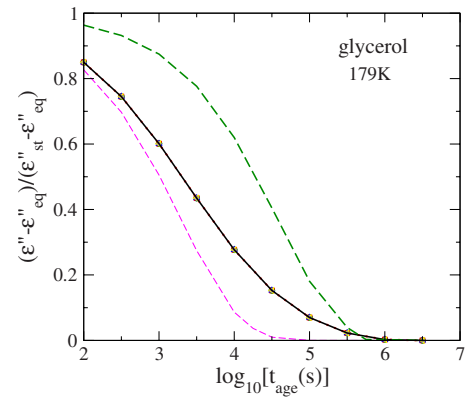

FIG. 4. (Color online) Scaling of the dielectric data for glycerol at 179 K corresponding to different frequencies. Fits obtained with $\tau_{age}(t_{age})$ in the modified KWW ansatz determined from (a) Eq. (4) of the present work (solid line) and (b) Ref. [5] (dashed line). Also shown are best fits obtained taking $\tau_{age}=\tau_{st}$ (short dashed) and $\tau_{age}=\tau_{eq}$ (long dashed), respectively, with the stretching exponent being fixed at β_α.

times, respectively equal to τ_{st} and τ_{eq}. The stretching parameter in both cases is β_α. The inadequacy of a simple KWW form in fitting the observed data is clearly observable here.

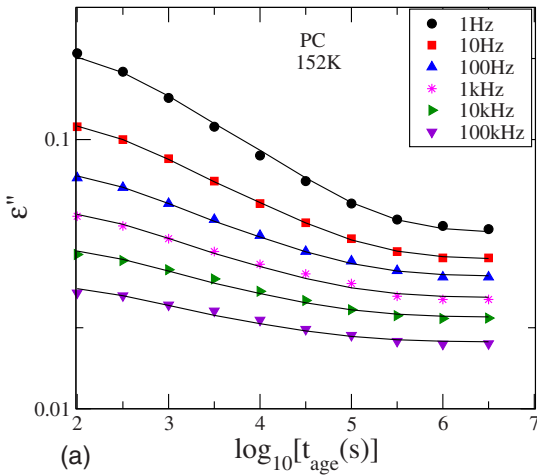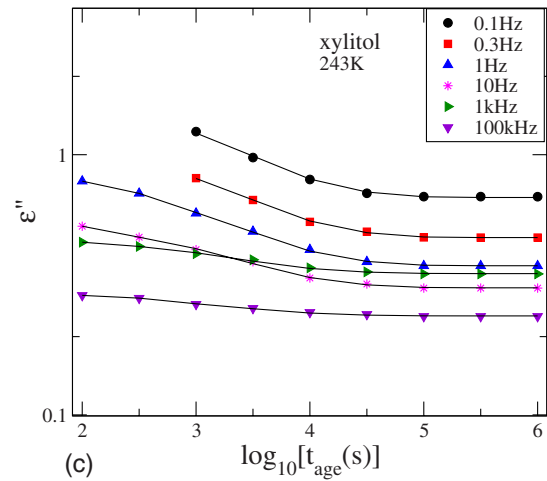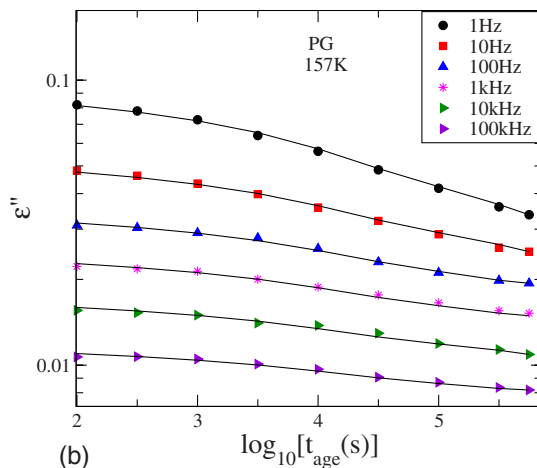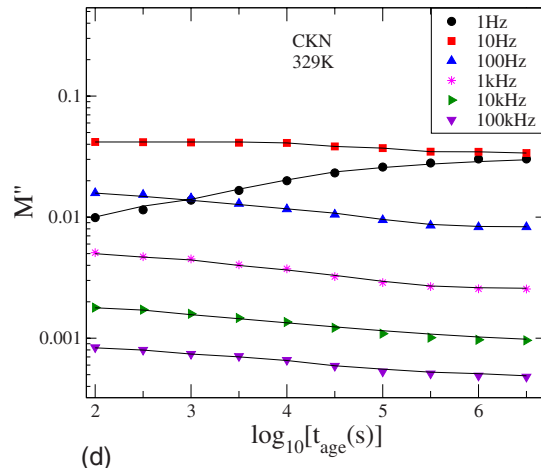In addition to the dielectric data for glycerol, following

FIG. 5. (Color online) (a) $\epsilon''(t_{age})$ data for PC [6,15] at 152 K vs t_{age} (s) at the frequencies displayed in the inset, (b) $\epsilon''(t_{age})$ data for PG [8,16] at 157 K(s) at the frequencies displayed in the inset, (c) $\epsilon''(t_{age})$ data for xylitol [16] at 243 K vs t_{age} (s) at the frequencies displayed in the inset, and (d) $M''(t_{age})$ data for CKN [18] at 329 K vs t_{age} (s) at the frequencies displayed in the inset. In all panels, the solid lines are obtained using our scheme.
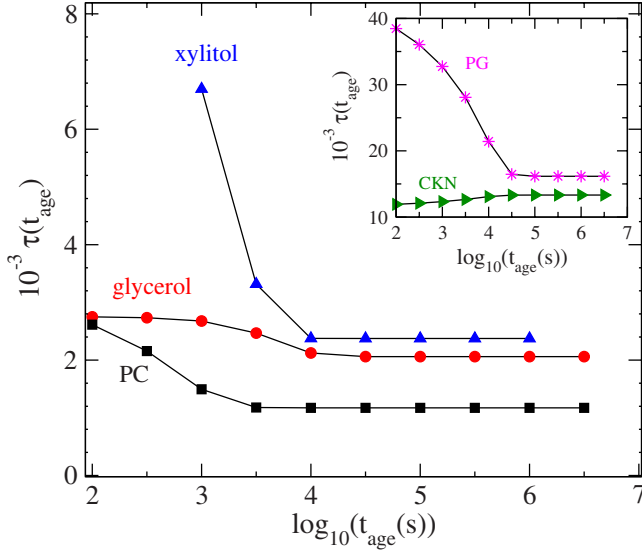
FIG. 6. (Color online) $\tau(t_{age})$ vs t_{age} (s) for different materials using ansatz (4) in the present work.
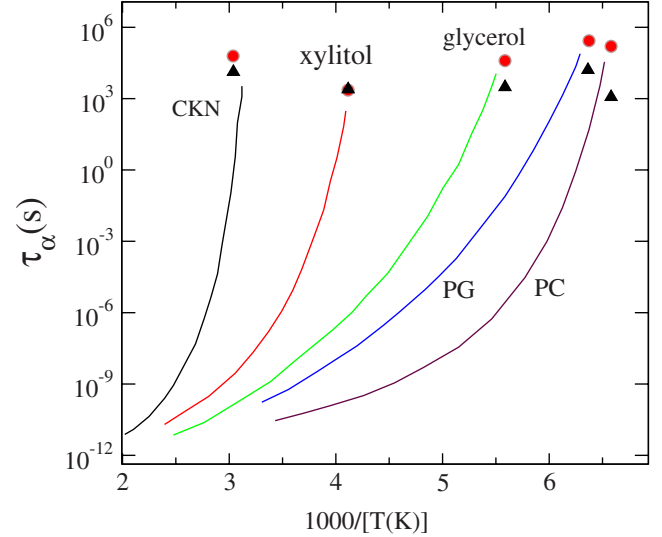

FIG. 7. (Color online) α-relaxation time τ_α vs inverse of temperature for CKN [6], xylitol [15], glycerol [16], PG [17], and PC [18]. The τ_{eq} obtained from the fitting of the corresponding data is shown by filled circles for the fitting of Ref. [5] and by filled triangles for the present fitting scheme.

Lunkenheimer *et al.*, we also fitted using our scheme the dielectric data for propylene carbonate (PC, $T_g \approx 159$ K, m =104 [8]), propylene glycol (PG, $T_g \approx 168$ K, m=52 [8]), and xylitol ($T_g \approx 248$ K, m=94 [13,14]) and structural relaxation for $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN, $T_g \approx 333$ K, m =93), and the results are shown, respectively, in Figs. 5(a)–5(d). The temperature (below the corresponding T_g in each case is also displayed in the figure. The variation of the relaxation time $\tau_{age}(t_{age})$ in the modified KWW form for fitting the data in each of the above materials is shown in Fig. 6. For all these materials, the general trend in aging time dependence of the relaxation time is the same as that in the case of glycerol. τ_{age} is strongly time dependent initially (up to time τ_{fn}) and finally saturates to an almost constant value, as is clearly visible in Fig. 6. Table I represents the stretching exponent β_{age} as a best-fit parameter in the aging data for different materials obtained from the present work (column 1) and also from Ref. [5] (column 2).

In case of the fitting scheme of Lunkenheimer *et al.*, the time scale τ_{eq} agrees with the extrapolated value of the α relaxation to the sub-T_g region. This is shown in Fig. 7 for all

TABLE I. The stretching exponent β_{age} as a best-fit parameter in the aging data for different materials obtained (a) from the present work (column 1) and (b) from Ref. [5] (column 2). The corresponding references from which the data for αrelaxation are taken are also provided in column 2

	Stretching exponent β_{age}	
Material	Present work	Ref. [5]
Glycerol	0.29	0.55 [5]
PC	0.24	0.6 [6,15]
PG	0.23	0.5 [16,17]
Xylitol	0.45	0.43 [16]
CKN	0.34	0.4 [18]

the five materials whose relaxation data have been considered above. First the τ_α's for these materials with inverse temperature $1/T$ are shown. On the same figure we display for each curve (with a filled circle) the corresponding value of $\tau_{eq}=1/(2\pi\nu_{eq})$ obtained from the best-fit value of (3) obtained by Lunkenheimer *et al.* These points all lie on the corresponding extrapolated curve of the α-relaxation times in the sub-T_g regime. These authors conclude that the equilibrium α relaxation is determining the aging process. On the other hand, the corresponding values of $\tau_{eq} \equiv \tau_{fn}$ obtained in our fitting scheme are shown for each curve with a filled triangle conforming to a relaxation mechanism of aging different from that of the equilibrium α relaxation.

We have presented here an alternative scenario for explaining the dielectric relaxation data of Lunkenheimer *et al.* [6] in the aging regime. The present model proposes that the aging process involves two basic steps. In the first stage, the aging data fit to a *modified* stretched exponential form with a time-dependent relaxation time τ_{age}. This is similar to the scheme of Lunkenheimer *et al.* but the time dependence of $\tau_{age}(t_{age})$ is more natural here. As t_{age} reaches a characteristic time scale τ_{fn}, the data can now be described in this second stage with a simple KWW form having a *constant* relaxation time comparable to τ_{fn}. This holds simultaneously for relaxation data at all frequencies as shown in Fig. 6. The limiting value of τ_{fn} obtained here from fitting the data is, however, *not* same as that obtained from extrapolation of α-relaxation times at higher temperatures to the sub-T_g region. The stretching exponent β_{age} is also very different from that of the α-relaxation process. The time dependence of the aging process and the corresponding relaxation time is possibly controlled by mechanisms that are different from that of equilibrium α relaxation.

The present analysis does not claim in any way that the fitting scheme proposed by Lunkenheimer *et al.* is invalid.

The main difference of the model proposed here from that in Ref. [5] lies in the manner in which the relaxation time τ_{age} depends on t_{age}. In our scheme the relaxation time τ_{age} is directly dependent on t_{age}. This is distinct from adopting the some what unusual scheme of (3) in which the time dependence is imposed via the frequency ν_{age}. The justification of this scheme in which the aging time dependence of τ_{age} is defined in terms of the frequency is not obvious. The motivation for adopting such a scheme is that the asymptotic value for τ_{age} (for long times) agrees with the value of the α-relaxation time at higher temperatures extrapolated to the sub-T_g region. There is no compelling reason to assume such a link between the nonequilibrium aging process and the equilibrium α relaxation.

To explain the last statement, let us consider the correlation function $\mathcal{C}(t+t_{\text{age}},t_{\text{age}})$ of fluctuations at two different times t_{age} and $t+t_{\text{age}}$. In the nonequilibrium state $\mathcal{C}$ depends on two times, i.e., both t and t_{age}. When time translational invariance holds, the dependence of $\mathcal{C}$ on t_{age} disappears. This happens over some time scale, which is τ_{eq}. The correlation function now depends only on t and the system has reached equilibrium. At this stage the relaxation is controlled by the α-relaxation time τ_α. But the time scale τ_{eq} which sets the dependence of the correlation function on t_{age} has no reason to be the same as τ_α. In other words, we insist that there is no *a priori* reason to assume that the time evolution of ϵ'' during the aging process in the nonequilibrium state is controlled by the equilibrium α-relaxation process and the corresponding heterogeneity. Our work clearly shows here that the dielectric data can also be fitted with the modified KWW form with a different choice for the aging time dependence of the corresponding relaxation time.

An important aspect of the proposed relaxation behavior lies in the different time evolution of the relaxation time τ in comparison to that of Ref. [5]. Here τ decreases with increasing waiting time t_{age}, implying that the aging process accelerates with time. It should, however, be noted that in the present case the relaxation time only decreases initially and then becomes almost constant. The stretching data at different frequencies correspond to a single relaxation time that is almost constant for aging time t_{age} beyond this initial scale τ_{fn}. The stretching exponent β_{age} for different frequency data is also the same. In Ref. [5] the relaxation time τ actually grows with waiting time. Though somewhat speculative at this stage, such a difference in the basic nature of the aging process might imply a different microscopic mechanism for aging altogether. The more appropriate choice between the two schemes (for fitting the aging data) discussed here can only be ascertained with a proper theoretical model for the evolution of the nonequilibrium state.

[1] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996); C. A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000).

[2] L. C. E. Struik, *Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).

[3] W. Kob and J. L. Barrat, Phys. Rev. Lett. **78**, 4581 (1997).

[4] L. F. Cugliandolo and J. Kurchan, Phys. Rev. Lett. **71**, 173 (1993).

[5] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Phys. Rev. Lett. **95**, 055702 (2005).

[6] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[7] C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (NRL, Washington, D.C., 1985), p. 3.

[8] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[9] R. L. Leheny and S. R. Nagel, Phys. Rev. B **57**, 5154 (1998).

[10] P. Lunkenheimer, R. Wehn, and A. Loidl, J. Non-Cryst. Solids **352**, 4941 (2006).

[11] V. S. Zotev, G. F. Rodriguez, G. G. Kenning, R. Orbach, E. Vincent, and J. Hammann, Phys. Rev. B **67**, 184422 (2003).

[12] A. Q. Tool, J. Am. Ceram. Soc. **29**, 240 (1946); O. S. Narayanaswamy, *ibid.* **54**, 491 (1971).

[13] A. Döß, M. Paluch, H. Sillescu, and G. Hinze, Phys. Rev. Lett. **88**, 095701 (2002).

[14] A. Döß, M. Paluch, H. Sillescu, and G. Hinze, J. Chem. Phys. **117**, 6582 (2002); A. Minoguchi, K. Kitai, and R. Nozaki, Phys. Rev. E **68**, 031501 (2003).

[15] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, Contemp. Phys. **41**, 15 (2000).

[16] R. Wehn *et al.* (unpublished).

[17] K. L. Ngai *et al.*, J. Chem. Phys. **115**, 1405 (2001).

[18] A. Pimenov, P. Lunkenheimer, H. Rall, R. Kohlhaas, A. Loidl, and R. Böhmer, Phys. Rev. E **54**, 676 (1996).