

# Physical Aging in Supercooled Glycerol: Evidence for Heterogeneous Dynamics?

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Several recent experiments on glycerol and other supercooled liquids have suggested that dynamically heterogeneous domains in the liquid are responsible for the nonexponential structural relaxation dynamics observed near the glass transition. In addition, it appears that the exchange of domain types may occur much more slowly than intradomain relaxation, at least in some cases. By examining a simple model of a dynamically heterogeneous liquid, we show that these ultraslow domain-exchange dynamics should be apparent at long times in nonequilibrium, physical aging experiments where the distribution of domains is perturbed. We recently observed such an ultraslow tail in the physical aging dynamics of the Brillouin shift for supercooled glycerol, following a rapid quench to a temperature below the glass transition (Miller, R. S.; MacPhail, R. A. *J. Chem. Phys.* **1997**, *106*, 3393); here we describe physical aging experiments carried out at two additional final temperatures. Unfortunately, the precision in the newer measurements at long times is not sufficient for us to resolve an ultraslow component. However, the broad distribution of relaxation times that characterizes the aging dynamics is consistent with the presence of such a tail and is much broader than the distribution for the equilibrium supercooled liquid. While our new experiments are ambiguous as to the nature of this broadening and the ultraslow tail, we believe the notion that the physical aging process can be sensitive to spatially heterogeneous dynamics is important, and we suggest further experiments designed to address this issue.

## Introduction

While much of the phenomenology of dynamics in supercooled liquids is well established, significant gaps remain.<sup>1,2</sup> For example, it is well-known that the slow structural relaxation dynamics of many supercooled liquids are distinctly nonexponential in time and non-Arrhenius in their temperature dependence. Indeed, Angell has shown how liquids can be classified according to their “fragility”, a measure of their deviation from the exponential, Arrhenius behavior observed at high temperatures and in “strong” liquids.<sup>2,3</sup> What has not been known is whether the nonexponential relaxation observed in fragile liquids results from a heterogeneous distribution of dynamics, likely associated with spatial heterogeneities in the liquid, or from inherently nonexponential, but spatially homogeneous, dynamics. An answer to this fundamental question would allow one to distinguish between many competing theories of supercooled liquids which predict nonexponential dynamics, but which start from distinctly different viewpoints regarding the presence of heterogeneities.<sup>1</sup> By analogy with line broadening in optical spectroscopy, the question is whether the distribution or “spectrum” of relaxation times associated with these nonexponential relaxation dynamics is a homogeneous or inhomogeneous distribution.

Quite recently, a number of experiments have begun to address this issue. For instance, it has been argued that the enhancement of translation diffusion relative to rotational relaxation observed in several fragile supercooled liquids can be rationalized if the dynamics are spatially heterogeneous.<sup>4,5</sup> A very recent simulation based on such a model lends strong support to this view<sup>6</sup> and further shows that most of the experimental enhancement data are consistent with a scenario where the interchange or exchange of dynamically different

regions occurs on a time scale considerably longer than the time scale for relaxation within the regions themselves; i.e., the relaxation spectrum is distinctly inhomogeneous. A similar conclusion was reached on the basis of optical-probe photobleaching experiments.<sup>7</sup> Here, a deep bleaching process was presumed to leave a nonequilibrium distribution of dynamical environments around the unbleached probes, and this distribution was observed to relax back to equilibrium on a time scale roughly 2 orders of magnitude longer than the average rotational correlation time. Four-dimensional nuclear magnetic resonance experiments on both polymers<sup>8</sup> and molecular liquids<sup>9</sup> have also been interpreted as indicating spatially heterogeneous dynamics, although in this case the time scale for interchange of the dynamical environments and the rotational correlation time were found to be similar. Rather direct evidence for dynamical heterogeneities was presented in another recent study where spectral holes were burned in the dielectric spectrum of two supercooled liquids, one of them glycerol.<sup>10</sup> The hole recovery time was comparable to the average dielectric relaxation time measured in the linear response regime, and this behavior was contrasted with the ultraslow recovery of the distribution of relaxation times observed in the photobleaching experiments. However, it was also noted that the hole in the dielectric spectrum maintained its shape during recovery, indicating that exchange between different “domains” was not important on the time scale for hole filling. Since it is this exchange which is presumably necessary for equilibration of the domain distribution in the deep photobleaching experiments, it would appear to us that the photobleaching and dielectric hole burning results both provide a consistent picture where domain-exchange dynamics are much slower than “intradomain” relaxation. It has also been inferred from some of these measurements<sup>7,8</sup> and others<sup>11–13</sup> that the characteristic length scale of dynamically heterogeneous domains is on the order of 1–10 nm near the glass transition. Taken collectively, these studies provide

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considerable support for the notion that dynamics in supercooled liquids near the glass transition are spatially heterogeneous on a nanometer length scale. Moreover, they suggest that the identity of the spatial domains responsible for the dynamical heterogeneity is maintained for times considerably longer than the average “intradomain” relaxation time, at least in some systems.

Nonequilibrium distributions of relaxation times can also be created and studied through more traditional “physical aging” experiments.<sup>1,14–19</sup> Such experiments typically involve creating an unstable, nonequilibrium state in the supercooled liquid through a temperature (or pressure) jump and then following the relaxation to equilibrium by monitoring some bulk property, like the density or enthalpy.<sup>14–19</sup> (Following common practice<sup>1</sup> we shall speak of an “equilibrium supercooled liquid”, even though such a system is metastable with respect to the crystal.) The initial nonequilibrium state is usually sufficiently far from equilibrium to be in a nonlinear regime, with the consequence that the average time scale for reaching equilibrium can be quite different from the average time scale for linear response dynamics in the final equilibrium state. Recent enthalpy relaxation measurements on several liquids including glycerol indicate that this nonlinearity also perturbs the width of the distribution of relaxation times characterizing the physical aging dynamics.<sup>18–20</sup> Thus, if the dynamics in the supercooled liquid are indeed spatially heterogeneous, one might expect both the intradomain and domain-exchange dynamics to be reflected in physical aging.

We have recently carried out a physical aging experiment in which the Brillouin shift of supercooled glycerol was monitored as a function of time following a rapid temperature quench from above to below the glass transition.<sup>21</sup> After a rapid, initial change in the Brillouin shift that tracked the temperature equilibration, we observed slow, nonexponential aging dynamics that appeared to contain an ultraslow component. We suggested this ultraslow tail might reflect the same kind of ultraslow domain-exchange dynamics discussed above and observed in the deep photobleaching experiments on *o*-terphenyl. Our purpose in the current article is to make the proposed connection between spatially heterogeneous dynamics and physical aging more explicit and to examine new data on the physical aging of glycerol for the presence of this ultraslow tail.

### Spatially Heterogeneous Dynamics and Physical Aging

We wish to describe the physical aging dynamics of a supercooled liquid with spatially heterogeneous dynamics. To make our argument concrete, we shall assume a particularly simple model, although we expect our general conclusions should be valid for other models as well. We picture the supercooled liquid as being composed of microscopic spatial domains within which the relaxation dynamics are exponential. The intradomain dynamics are characterized by a relaxation time  $\tau(\Omega)$  which is controlled by some spatially varying variable or set of variables  $\Omega$ . (For example,  $\Omega$  might correspond to the local density<sup>7</sup> or configurational entropy<sup>12</sup> within a domain.) The equilibrium distribution of relaxation times is then determined by the equilibrium distribution of  $\Omega$  values  $P_{\text{eq}}(\Omega)$  and the functional dependence of  $\tau$  on  $\Omega$ . We also incorporate a second time scale  $\tau_{\text{ex}}$  which characterizes the domain-exchange dynamics. For simplicity, we assume that if the distribution of  $\Omega$  values and relaxation times is perturbed, it will relax exponentially to the equilibrium distribution with time constant  $\tau_{\text{ex}}$ . We note that this model is very similar to the one examined by Ediger and co-workers<sup>6</sup> in their simulations of translational motion in a medium with spatially heterogeneous dynamics.

We are interested in the physical aging of a macroscopic observable  $A(t)$  which is an average over the values of the corresponding microscopic variable  $a(\Omega, t)$  in the different domains. We assume the effect of a temperature jump (or other perturbation) is to leave the system, after rapid equilibration to the new temperature, in a state where both the distribution of  $\Omega$  values  $P(\Omega, t)$  and the value of  $a(\Omega, t)$  in the domains are perturbed. Thus, we can express the time dependence of the macroscopic variable  $A(t)$  as

$$A(t) = \int d\Omega P(\Omega, t) a(\Omega, t) \\ = \int d\Omega \{P_{\text{eq}}(\Omega) + \delta P(\Omega) \exp(-t/\tau_{\text{ex}})\} \{a(\Omega) + \delta a(\Omega) \exp[-t/\tau(\Omega)]\} \quad (1)$$

where in the second line we have separated out the amplitudes  $\delta P(\Omega)$  and  $\delta a(\Omega)$  and time dependences of the relaxing parts of  $P(\Omega, t)$  and  $a(\Omega, t)$ , respectively. Note that  $P_{\text{eq}}(\Omega)$  is the equilibrium distribution in the final state, i.e., at the final temperature in a temperature quench. The various terms in eq 1 can be recombined in the more illuminating form:

$$A(t) = \int d\Omega P_{\text{eq}}(\Omega) a(\Omega) + \int d\Omega \{P_{\text{eq}}(\Omega) + \delta P(\Omega) \exp(-t/\tau_{\text{ex}})\} \delta a(\Omega) \exp[-t/\tau(\Omega)] + \int d\Omega \{\delta P(\Omega) \exp(-t/\tau_{\text{ex}})\} a(\Omega) \quad (2)$$

We are especially interested in the limit where the domain-exchange dynamics are much slower than the intradomain dynamics, i.e., where  $\tau_{\text{ex}} \gg \tau(\Omega)$  for relevant values of  $\Omega$ . In this limit eq 2 simplifies further since the time dependence of the exchange dynamics in the second integral on the right-hand side can be neglected, leaving

$$A(t) \approx A_{\text{eq}} + \int d\Omega \{P_{\text{eq}}(\Omega) + \delta P(\Omega)\} \delta a(\Omega) \times \exp[-t/\tau(\Omega)] + \exp(-t/\tau_{\text{ex}}) \int d\Omega \delta P(\Omega) a(\Omega) \quad (3)$$

where we have identified the first integral on the right-hand side of eq 2 with  $A_{\text{eq}}$ , the equilibrium value of  $A$  at the final temperature. This equation predicts that the physical aging dynamics for such a system should proceed in two stages. The first stage, given by the first integral on the right-hand side of eq 3, corresponds to relaxation within the domains, but with a perturbed distribution of domains and relaxation times that is approximately static. The second stage, given by the second integral on the right-hand side of eq 3, corresponds to ultraslow relaxation of the distribution itself via domain-exchange dynamics.

Several comments on eqs 2 and 3 are in order. First, we note that, in the linear response limit where  $\delta P(\Omega) \rightarrow 0$ , the dynamics are controlled by the equilibrium distribution  $P_{\text{eq}}(\Omega)$  alone and the ultraslow term vanishes, as expected. Second, we do not necessarily expect eq 2 to be accurate when  $\tau_{\text{ex}}$  becomes comparable to  $\tau(\Omega)$ , since in this case the domain-exchange dynamics will be folded into the overall distribution of relaxation times in a more complex way, as observed in the simulations by Ediger and co-workers.<sup>6</sup> Third, we can see from the last term in eq 3 that different physical observables may show different sensitivities to the domain-exchange dynamics depending on the sensitivity of  $a(\Omega)$  to  $\Omega$ . In fact, for the case where  $a(\Omega)$  is independent of  $\Omega$  the last term will vanish, since the normalization conditions for  $P_{\text{eq}}(\Omega)$  and  $P(\Omega, t)$  require that the integral  $\int d\Omega \delta P(\Omega) = 0$ .

Equation 3 can be recast in a form more suitable for fitting experimental data if we assume the intradomain dynamics (first integral on the right-hand side of eq 3) can be approximated by a stretched exponential  $\exp[-(t/\tau_S)^{\beta_S}]$  and the rapid initial dynamics (not included in eq 3) by a simple exponential  $\exp(-t/\tau_T)$ , where  $\tau_T$  is the time constant for temperature equilibration. In this case the time dependence of  $A(t)$  would have the form

$$A(t) \approx A_{eq} + \delta A_F \exp(-t/\tau_T) + \delta A_S \exp[-(t/\tau_S)^{\beta_S}] + \delta A_U \exp(-t/\tau_{ex}) \quad (4)$$

where  $\delta A_F$ ,  $\delta A_S$ , and  $\delta A_U$  are the amplitudes of contributions to  $A(t)$  which relax during the fast temperature equilibration period, by slow intradomain relaxation, and by ultraslow domain-exchange dynamics, respectively. In our previous study of physical aging in glycerol we found empirically that an equation of this functional form gave a good representation of our Brillouin shift data.<sup>21</sup> Depending on the precision of the aging measurement and on the magnitude of the perturbation and the amplitude  $\delta A_U$ , it may be difficult to resolve the ultraslow term in eq 4 in real data. In such a case, one might expect that a single stretched exponential could approximately describe both of the last two terms in eq 4, i.e.

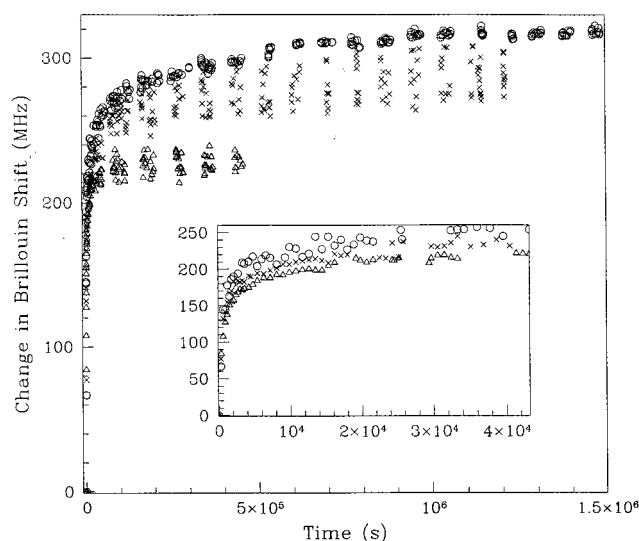
$$A(t) \approx A_{eq} + \delta A_F \exp(-t/\tau_T) + \delta A \exp[-(t/\tau)^{\beta}] \quad (5)$$

and that  $\beta \leq \beta_S$  and  $\tau \geq \tau_S$  since the stretched exponential in eq 5 would be forced to describe an effective distribution of relaxation times broadened and shifted to longer times by the incorporation of the ultraslow term in eq 4. Our new aging data may be an example where this is indeed the case.

Before proceeding with an analysis and discussion of the experimental results, we also wish to comment on the generality of the above picture. The expressions in eqs 2–4 were rationalized on the basis of one particularly simple model of spatially heterogeneous dynamics in supercooled liquids, and there is no strong evidence to suggest that this model is uniquely correct. Indeed, a number of different models of heterogeneous dynamics in supercooled liquids have been proposed. For example, some have postulated the presence of solidlike and liquidlike regions in the fluid or two-fluid models,<sup>22,23</sup> where the heterogeneities are related to differences in free volume or structure in the different regions, while others have suggested that heterogeneities result from variations in the sizes of the domains.<sup>24,25</sup> The heterogeneities can give rise to nonexponential dynamics in the equilibrium supercooled liquid in different ways as well, for example, from the presence of diffusing “defects”<sup>23,26</sup> or more directly from the distribution of domain sizes or properties.<sup>6,12,13,24,25</sup> Despite these differences, such models generally admit the possibility that changes in the distribution of relaxation times during physical aging could occur on an “ultraslow” time scale, for example, through a change in the concentration of diffusing defects or the restructuring of domain walls. Thus, while the detailed nature of the motions responsible for dynamics we have associated with “intradomain relaxation” or “domain-exchange” might differ among these models, we still expect our general argument leading to the two-stage physical aging dynamics described in eqs 3 and 4 to remain valid.

## Experimental Section

The two new physical aging experiments reported here were carried out in exactly the same manner as the one described in our previous study,<sup>21</sup> the only difference being the initial and



**Figure 1.** Change in the Brillouin frequency shift versus time for physical aging experiments at three different final temperatures: (O)  $T_{\text{final}} = 179.8$  K, ( $\times$ )  $T_{\text{final}} = 181.4$  K, ( $\Delta$ )  $T_{\text{final}} = 184.0$  K. The inset shows an expanded view of the short time (to 12 h) behavior.

**TABLE 1: Values<sup>a</sup> of Parameters Resulting from Fits of Eq 6 to Brillouin Shift Data for Three Aging Experiments with Different Final Temperatures**

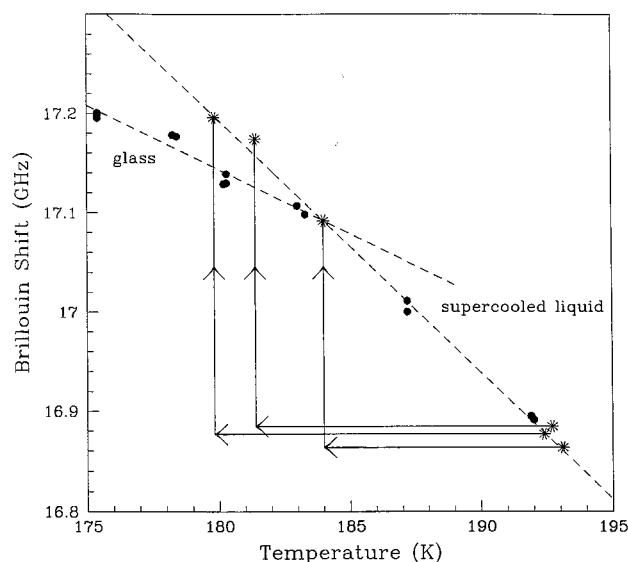
$T_{\text{final}}$ (K)	179.8	181.4	184.0
$T_{\text{initial}}$ (K)	192.4	192.7	193.1
$\Delta\omega_B(t=\infty)$ (MHz)	$331 \pm 4$	$292 \pm 4$	$228 \pm 1$
$\delta\omega_F$ (MHz)	$144 \pm 10$	$90 \pm 20$	$60 \pm 10$
$\tau_F$ (ks)	$0.46 \pm 0.03$	$0.65 \pm 0.04$	$0.65 \pm 0.03$
$\delta\omega$ (MHz)	$200 \pm 20$	$200 \pm 30$	$170 \pm 20$
$\tau$ (ks)	$48 \pm 7$	$17 \pm 7$	$2.6 \pm 0.5$
$\beta$	$0.30 \pm 0.03$	$0.28 \pm 0.04$	$0.38 \pm 0.02$

<sup>a</sup> The uncertainties given correspond to the standard errors for the parameters estimated from the goodness of fit.

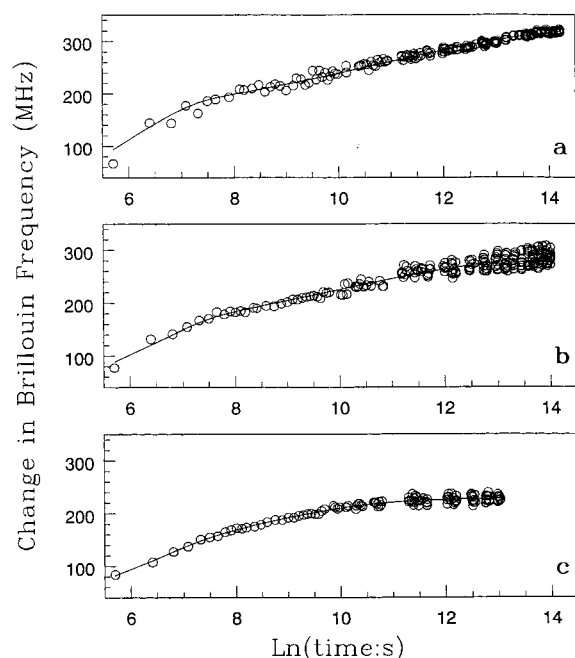
final temperatures. The glycerol sample and sample cell were the same, and the temperature control was achieved in the same manner. As before, the physical aging was monitored by collecting Brillouin spectra as a function of time with our stimulated Brillouin gain spectrometer,<sup>27</sup> and the operating parameters for the spectrometer and method of extracting the Brillouin frequency shift and line width from the spectra were identical with those described previously.<sup>21</sup> The quality of the spectra measured in the new experiments was comparable to the spectra shown in our earlier work.<sup>21</sup> The reader is referred elsewhere for additional details.<sup>21,27</sup>

## Results and Discussion

Figure 1 shows the change in Brillouin frequency shift of supercooled glycerol as a function of time for three different physical aging experiments, the one described previously<sup>21</sup> and two new ones. The Brillouin shift measured in these experiments corresponds to the frequency of longitudinal acoustic phonons with an acoustic wavelength of approximately  $0.2 \mu\text{m}$ ,<sup>21,29</sup> and the changes observed represent changes in the speed of sound (which depends on the longitudinal elastic modulus and the density) and also in the scattering wavevector through its dependence on the index of refraction. In each experiment, the sample was first allowed to equilibrate for 24 h at an initial temperature  $T_{\text{initial}}$  near 193 K (see Table 1), where the Brillouin shift is 16.9 GHz.<sup>21</sup> The temperature was then allowed to drop rapidly to a final temperature  $T_{\text{final}}$ ; for the two new experiments  $T_{\text{final}} = 181.4$  and 184.0 K, and for the earlier experiment  $T_{\text{final}} = 179.8$  K. See Figure 2.



**Figure 2.** Brillouin frequency shift versus temperature. The circles are the experimental points from ref 21 that were obtained on slow cooling, with the dashed lines representing linear fits to the data above and below the glass transition. The asterisks show the initial and final measured values of the Brillouin shift for each of the three aging experiments in Figure 1, and the arrows indicate the associated changes in temperature and Brillouin shift.



**Figure 3.** Change in the Brillouin frequency shift versus the natural logarithm of time for physical aging experiments at three different final temperatures: (a)  $T_{\text{final}} = 179.8$  K, (b)  $T_{\text{final}} = 181.4$  K, (c)  $T_{\text{final}} = 184.0$  K. The solid lines are the fits to eq 6.

As can be seen from Figure 1, in all three cases the Brillouin shift shows a rapid initial response which tracks the equilibration of the temperature, followed by a slower physical aging response. As expected, both the magnitude of the total change in Brillouin shift and the time for the Brillouin shift to reach equilibrium increase with decreasing  $T_{\text{final}}$ . (In all three experiments we collected data until the Brillouin shift had fully relaxed to the value expected for the equilibrium supercooled state at  $T_{\text{final}}$ , as determined from previous measurements of the Brillouin shift versus temperature in the equilibrium supercooled liquid above the glass transition.<sup>21</sup> See also Figure 2.) Figure 3 shows the same data plotted versus  $\ln(\text{time})$ , a representation which is

convenient because it expands the data points at short times and compresses them at long times. The change in slope near  $\ln(\text{time/s}) \approx 7.5$  in each of the plots in Figure 3 corresponds to the crossover from the rapid initial response to the slower physical aging response. As in our earlier aging experiment,<sup>21</sup> the Brillouin line widths in the two new experiments showed a rapid response as the temperature equilibrated but then remained constant during the slow aging period (at a value of  $18 \pm 3$  MHz).

It is evident from Figures 1 and 3 that the precision in the Brillouin shift measurements differed considerably among the three aging experiments. At shorter times the precision in the new measurements with  $T_{\text{final}} = 181.4$  and  $184.0$  K is actually better than in the earlier experiment with  $T_{\text{final}} = 179.8$  K; see the inset in Figure 1 and the data for  $\ln(\text{time/s}) \leq 10$  in Figure 3. However, at the long times the precision is considerably worse, with the rms deviations in the shift measurements at long times being  $\pm 13$ ,  $\pm 6$ , and  $\pm 3$  MHz for the experiments with  $T_{\text{final}} = 181.4$ ,  $184.0$ , and  $179.8$  K, respectively. This loss in precision at long times is unfortunate since this is exactly where we would expect to observe the ultraslow tail associated with "domain-exchange" dynamics, if it exists. The precision of our measurements depends critically on the alignment and stability of the ring dye-laser in our apparatus,<sup>27</sup> and we believe the degradation in precision observed over the several day course of the new aging experiments resulted from a gradual loss in the frequency stability of the dye laser. Maintaining the laser stability and precision throughout these long experiments is clearly a challenge for future measurements of physical aging with this technique.

To characterize the aging dynamics in a more quantitative fashion, we have used analogues of eqs 4 and 5 to fit the Brillouin shift data. For our previous experiment with  $T_{\text{final}} = 179.8$  K, we found that explicit inclusion of the ultraslow term in eq 4 led to a significant improvement in the fit over the simpler model in eq 5, reducing the sum of squared errors by 25%.<sup>21,28</sup> However, for the two new experiments at  $T_{\text{final}} = 181.4$  and  $184.0$  K no such improvement was found, and the sum of squared errors was essentially the same whether the ultraslow term was included in the fitting model or not. Clearly, use of the more complicated fitting model (i.e., eq 4) is not justified for the new experiments because of the poorer precision in the long time data. Thus, to characterize the new aging experiments and compare them with the previous experiment on a common basis, all three sets of data were fit with the simpler model of eq 5, more specifically with the form

$$\Delta\omega(t) = \Delta\omega(t=\infty) - \delta\omega_F \exp[-t/\tau_F] - \delta\omega \exp[-(t/\tau)^\beta] \quad (6)$$

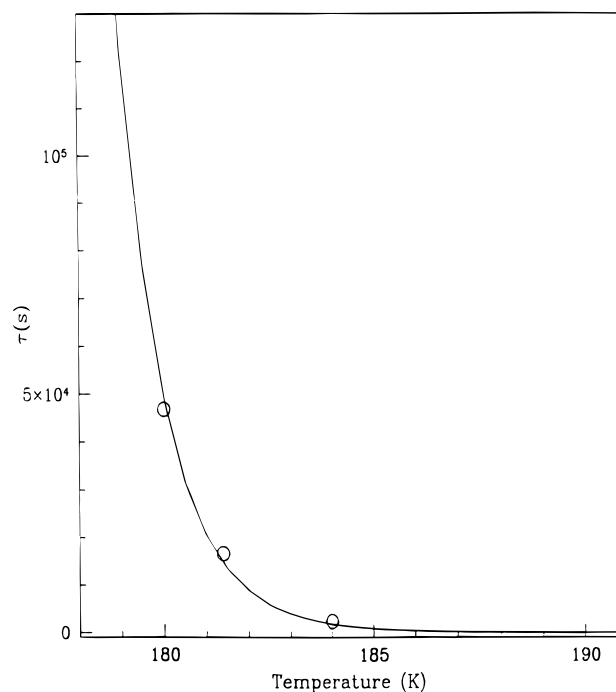
where  $\Delta\omega(t)$  is the change in the Brillouin shift with time and  $\Delta\omega(t=\infty)$  is its value in the fully equilibrated final state and where the parameters  $\delta\omega_F$  and  $\delta\omega$  characterize the amplitudes of the fast and slow physical aging responses. The results of these fits are shown as solid lines in Figure 3, and the values of the parameters in eq 6 determined from the fits are listed in Table 1.

Several comments on the values of the parameters in Table 1 are in order. First, the values of  $\Delta\omega(t=\infty)$  match closely (within a few megahertz) those predicted from the temperature dependence of the Brillouin shift measured in the equilibrium supercooled liquid just above the glass transition (see Figure 2),<sup>21,29</sup> giving us confidence that we have indeed waited long enough to achieve full equilibrium in all three aging experiments. Second, the values of the time constant  $\tau_F$  for the rapid response in the Brillouin shift are identical with those determined

directly from the observed time dependences of the temperature relaxation. Third, the values of  $\tau$  display the dramatic temperature dependence expected near the glass transition, increasing by a factor of 20 as  $T_{\text{final}}$  decreases from 184.0 to 179.8 K. Finally, the  $\beta$  values of 0.3–0.4 are much smaller than the corresponding values of 0.65–0.67 determined for supercooled glycerol at equilibrium and in the same temperature regime through dielectric<sup>30</sup> and enthalpy<sup>18,19,31,32</sup> relaxation measurements. This clearly indicates that the effective distribution of relaxation times for the aging dynamics in our experiments is much broader than the equilibrium distribution of relaxation times at  $T_{\text{final}}$ . It is difficult to say on the basis of only these three experiments whether the higher value of  $\beta$  for the shallowest temperature quench ( $T_{\text{final}} = 184.0$  K) simply reflects the uncertainty in  $\beta$  or whether it indicates the trend observed in the enthalpy relaxation measurements,<sup>18,19</sup> where  $\beta$  increased toward the equilibrium value with decreasing quench depth.

What do the results of these fits say about the existence of an ultraslow tail in the physical aging dynamics? While no ultraslow tail could be resolved in our two new experiments, the small values of  $\beta$  are nearly the same as the value determined for the  $T_{\text{final}} = 179.8$  K experiment, where an alternate fit to an equation with the form of eq 4 indicated a statistically significant ultraslow tail with  $\tau_{\text{ex}} \approx 40 \tau_{\text{S}}$  (and  $\beta_{\text{S}} \approx 0.6$ ).<sup>21</sup> This similarity in  $\beta$  values indicates a similarly broad effective distribution of relaxation times for all three experiments, consistent with the presence of an ultraslow tail in the two new experiments as well.

To say more about the origin of this broadening without additional experiments of our own, we are forced to compare our results with those from other equilibrium and nonequilibrium experiments on glycerol (bearing in mind that differences in water content in the glycerol samples or in temperature calibration can make such comparisons problematic). In particular, we would like to determine from this comparison whether the broadening of the relaxation time distribution in our aging experiments is indicative of spatially heterogeneous dynamics and an accompanying ultraslow tail or whether it simply reflects the nonlinearity of the aging process. For a downward jump in temperature, conventional arguments on the effect of nonlinearity predict that the time scale for physical aging should be shorter than for relaxation in the linear response regime at the final equilibrium temperature.<sup>14–17</sup> And as mentioned in the Introduction, the nonlinearity apparently affects the width of the distribution of relaxation times as well, broadening the distribution in the case of a downward jump in temperature.<sup>18–20</sup> Thus, if we were to characterize the aging dynamics and the equilibrium dynamics by the stretched exponentials  $\exp[-(t/\tau)^\beta]$  and  $\exp[-(t/\tau_{\text{eq}})^{\beta_{\text{eq}}}]$ , respectively, then we would anticipate that nonlinearity alone would lead to  $\tau < \tau_{\text{eq}}$  (faster relaxation) and  $\beta < \beta_{\text{eq}}$  (broader distribution) for a downward jump in temperature. On the other hand, if the dynamics are spatially heterogeneous and contribute an additional ultraslow “domain-exchange” tail to the aging dynamics with  $\tau_{\text{ex}} > \tau_{\text{eq}}$ , as in eq 4, then one would expect further broadening of the effective distribution of relaxation times, but now to times longer than the equilibrium relaxation time. Thus, provided the magnitudes of the temperature jump and the ultraslow tail are sufficiently large, one might expect  $\tau \geq \tau_{\text{eq}}$  and  $\beta < \beta_{\text{eq}}$  as a signature of spatially heterogeneous dynamics. To summarize, both the nonlinearity of physical aging and the presence of an ultraslow tail associated with spatially heterogeneous relaxation are expected to broaden the effective distribution of relaxation times relative to the equilibrium distribution ( $\beta < \beta_{\text{eq}}$ ), but in the case of nonlinearity the



**Figure 4.** Characteristic relaxation times  $\tau$  obtained from fits of eq 6 to the Brillouin aging data versus  $T_{\text{final}}$ . The solid line shows the temperature dependence predicted for the corresponding equilibrium dielectric relaxation time from the data of ref 30.

distribution should be shifted to shorter times ( $\tau < \tau_{\text{eq}}$ ), whereas an ultraslow tail would contribute additional broadening toward longer times (potentially yielding  $\tau \geq \tau_{\text{eq}}$ ).

Perhaps the best equilibrium results for comparison are those obtained by Menon et al.<sup>30</sup> from dielectric relaxation measurements carried out over an extremely wide frequency range and at temperatures as low as 184 K. Interestingly, the values of  $\tau$  determined from our three aging runs track closely the temperature dependence of the corresponding equilibrium values determined from the dielectric spectrum peak frequency and are even close numerically at each temperature, as shown in Figure 4. (For this plot the dielectric relaxation time was taken to be  $0.8(2\pi\nu_p)^{-1}$ , where  $\nu_p(T)$  is the Vogel–Tamman–Fulcher function determined in ref 30 from the temperature dependence of the peak frequency and where the factor 0.8 corrects the time calculated from the peak frequency to the corresponding stretched exponential time constant  $\tau$  according to the prescription of Lindsey and Patterson.<sup>33</sup>) This agreement is especially remarkable given the large differences in  $\beta$  values between our aging results and the equilibrium dielectric results, 0.3 versus 0.65, respectively. (While it is not unusual for the dielectric spectra of supercooled liquids to be narrower than the corresponding acoustic or mechanical spectra, such differences in width are much smaller than the difference in  $\beta$  values observed here would imply.) Taken together, this comparison of  $\tau$  and  $\beta$  values suggests an effective distribution of relaxation times for the aging experiment that is much broader than the equilibrium distribution and skewed toward both shorter and longer relaxation times. Such a distribution would be entirely consistent with the expectations for spatially heterogeneous dynamics outlined above; as in eq 4, the ultraslow domain-exchange dynamics would broaden the distribution to longer times ( $\tau_{\text{ex}} \gg \tau_{\text{eq}}$ ) and the (nonlinear) slow intradomain relaxation would broaden the distribution to shorter times ( $\tau_{\text{S}} < \tau_{\text{eq}}$ ;  $\beta_{\text{S}} < \beta_{\text{eq}}$ ).

A comparison with the physical aging studies of Fujimori and Oguni<sup>18</sup> yields a more ambiguous conclusion. These

workers used enthalpy relaxation to monitor the physical aging of glycerol at 182 K for temperature jumps of different sizes  $\Delta T$ , but with a maximum  $\Delta T$  of 2 K, considerably smaller than the  $\Delta T$  range of 9–13 K in our experiments. (We restrict our attention here to downward temperature quenches such as ours, although Fujimori and Oguni also studied physical aging after upward temperature jumps.) They found that the observed aging dynamics could be well described by a single stretched exponential as in eq 5 and that the values of  $\tau$  and  $\beta$  increased with decreasing  $\Delta T$ . An extrapolation of their  $\beta$  values to  $\Delta T = 0$  gave a value of 0.67, in agreement with the value obtained from equilibrium measurements,<sup>30–32</sup> but extrapolation of their  $\tau$  values to  $\Delta T = 0$  gives approximately 30 ks, 3 times larger than the equilibrium  $\tau$  value predicted at 182 K from the dielectric measurements.<sup>30</sup> On comparing their values of  $\tau = 21$  ks and  $\beta = 0.56$  for  $\Delta T = 2$  K and  $T_{\text{final}} = 182$  K with our values of  $\tau = 17$  ks and  $\beta = 0.28$  for  $\Delta T = 11.3$  K and  $T_{\text{final}} = 181.4$  K, one might conclude that our results simply reflect an extension of the trend they see; i.e., they reflect the nonlinearity of aging but do not necessarily indicate the presence of an ultraslow tail. However, the discrepancy in the equilibrium  $\tau$  values between the enthalpy relaxation and dielectric results, and the closeness with which our  $\tau$  values track the latter (Figure 4), raise doubts about this comparison. In addition, Fujimori and Oguni apparently did not follow the physical aging dynamics of the enthalpy all the way to equilibrium, but ended their data collection at 75 ks.<sup>18</sup> If the ultraslow tail ( $\tau_{\text{ex}}$ ) is indeed an order of magnitude or more slower than the intradomain dynamics ( $\tau_{\text{s}}$ ), as our data at  $T_{\text{final}} = 179.8$  K suggest,<sup>21</sup> then they would have missed the ultraslow contribution to the aging dynamics, assuming it had sufficient amplitude to be observed in a jump of  $\Delta T \leq 2$  K.

We should also caution that even if we accept the ultraslow tail in our physical aging experiments as real, it could still have origins in phenomena other than the domain-exchange dynamics discussed earlier. For example, we pointed out previously that an ultraslow tail might also arise from slowly relaxing mechanical strain generated in the sample by the difference in thermal expansivities of the glycerol sample and glass sample cell.<sup>21</sup>

Clearly, additional experiments will be required to definitively establish the presence, or lack of, an ultraslow component in physical aging and to identify its origins. These experiments might best be patterned after those of Fujimori and Oguni,<sup>18,19</sup> i.e., characterizing the aging dynamics for temperature jumps of different depths to a single final temperature, but they should be extended to a larger range of jump sizes  $\Delta T$  and the dynamics should be followed until the sample has fully relaxed in order to capture any ultraslow contributions. Such experiments could be carried out for a variety of observables but would require high-precision measurements. It would also be valuable to carry out experiments on other supercooled liquids, particularly more fragile liquids where nonlinearities in the aging dynamics should be enhanced. Of these, *o*-terphenyl might be the system of choice, since both “enhanced translation diffusion” and photobleaching experiments on *o*-terphenyl strongly suggest the presence of spatially heterogeneous dynamics and ultraslow domain-exchange dynamics and in addition provide a time scale for the latter that can be compared with aging dynamics.<sup>6,7</sup>

## Conclusions

We have examined a simple model of a supercooled liquid with spatially heterogeneous dynamics and concluded that the physical aging dynamics of such a system should reflect both domain-exchange and intradomain relaxation processes if the

aging dynamics are sufficiently nonlinear to perturb the distribution of domains. In the limit where the domain-exchange dynamics are much slower than intradomain relaxation, the two contributions should be discernible in the aging dynamics, with the domain-exchange process contributing an ultraslow tail, much like the one we observed previously in the aging of the Brillouin shift for glycerol.<sup>21</sup> Recent dielectric hole burning and enthalpy relaxation experiments on glycerol<sup>9,18</sup> clearly establish the heterogeneous and nonlinear nature of the structural relaxation dynamics in glycerol, two of the necessary ingredients for our argument to hold. While the two new aging experiments on glycerol described here do not have sufficient precision at long times to identify a distinct tail, the breadth of the effective distribution of relaxation times is comparable to that in our previous study and is therefore consistent with the presence of such a tail. A comparison with the results of equilibrium dielectric relaxation measurements<sup>30</sup> suggests that the much broader distribution of relaxation times in the aging experiments may indeed be associated with the kind of two-stage relaxation dynamics we have predicted; a similar comparison with non-equilibrium enthalpy relaxation studies<sup>18</sup> on glycerol is equivocal on this point. Additional experiments that would clarify the presence and origin of the ultraslow tail are suggested.

At minimum, our experimental results support the conclusion of Fujimori and Oguni<sup>18,19</sup> that nonlinearities in the physical aging process affect both the average relaxation time *and the shape of the distribution of relaxation times*; while the former observation is well documented and has been treated phenomenologically, the latter has not been generally recognized.<sup>14–17</sup> Our results suggest that aging dynamics in supercooled liquids may be even richer and more informative, possibly reflecting details of spatially heterogeneous dynamics in a way that would not be observable in equilibrium dynamical measurements carried out in the linear response regime. We hope these results will encourage others to examine closely physical aging dynamics with high-precision measurements. The observation of an ultraslow tail in the aging dynamics would lend further support the idea that slow dynamics in supercooled liquids near glass transition are spatially heterogeneous. In addition, this observation could have important practical implications since physical aging can play a crucial role in the design and applications of amorphous materials.<sup>14–17</sup>

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## References and Notes

- Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, *100*, 13200.
- Angell, C. A. *Science (Washington, D.C.)* **1995**, *267*, 1924.
- Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
- Blackburn, F. R.; Wang, C.-Y.; Ediger, M. D. *J. Phys. Chem.* **1996**, *100*, 18249.
- Heuberger, G.; Sillescu, H. *J. Phys. Chem.* **1996**, *100*, 15255.
- Cicerone, M. T.; Wagner, P. A.; Ediger, M. D. *J. Phys. Chem.*, submitted.
- Cicerone, M. T.; Ediger, M. D. *J. Chem. Phys.* **1995**, *103*, 5684.
- Heuer, A.; Wilhelm, M.; Zimmermann, H.; Spiess, H. *Phys. Rev. Lett.* **1995**, *75*, 2851.
- Böhmer, R.; Hinze, G.; Diezemann, G.; Sillescu, H. *Europhys. Lett.* **1996**, *36*, 55.
- Schiener, B.; Böhmer, R.; Loidl, A.; Chamberlin, R. V. *Science (Washington, D.C.)* **1996**, *274*, 752.
- Donth, E. *J. Non-Cryst. Solids* **1982**, *53*, 325.
- Moynihan, C. T.; Schroeder, C. T. *J. Non-Cryst. Solids* **1993**, *160*, 52.
- Mohanty, U. *J. Chem. Phys.* **1994**, *100*, 5905.

- (14) Hodge, I. M. *Science (Washington, D.C.)* **1995**, 267, 1945.
- (15) Hodge, I. M. *J. Non-Cryst. Solids* **1994**, 169, 211.
- (16) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier Scientific: New York, 1978.
- (17) McKenna, G. B. *Comprehensive Polymer Science*; Booth, C., Price C., Eds.; Pergamon: Oxford, 1990; Vol. 2.
- (18) Fujimori, H.; Oguni, M. *J. Non-Cryst. Solids* **1994**, 172–174, 601.
- (19) Fujimori, H.; Fujita, H.; Oguni, M. *Bull. Chem. Soc. Jpn.* **1995**, 68, 447.
- (20) Moynihan, C. T.; Crichton, S. N.; Opalka, S. M. *J. Non-Cryst. Solids* **1991**, 131–133, 420.
- (21) Miller, R. S.; MacPhail, R. A. *J. Chem. Phys.* **1997**, 106, 3393.
- (22) Grest, G. S.; Cohen, M. H. *Adv. Chem. Phys.* **1981**, 48, 454.
- (23) Bendler, J. T.; Shlesinger, M. F. *J. Phys. Chem.* **1992**, 96, 3970.
- (24) Chamberlin, R. V.; Kingsbury, D. W. *J. Non-Cryst. Solids* **1994**, 172–174, 601.
- (25) Kivelson, D.; Kivelson, S. A.; Zhao, X.; Nussinov, Z.; Tarjus, G. *Physica A* **1995**, 219, 27.
- (26) Harrowell, P. *Phys. Rev. E* **1993**, 48, 4359.
- (27) Grubbs, W. T.; MacPhail, R. A. *Rev. Sci. Instrum.* **1994**, 65, 34.
- (28) Miller, R. S. Ph.D. Dissertation, Duke University, 1996.
- (29) Grubbs, W. T.; MacPhail, R. A. *J. Chem. Phys.* **1994**, 100, 2561.
- (30) Menon, N.; O'Brien, P.; Dixon, P. K.; Wu, L.; Nagel, S. R.; Williams, B. D.; Carini, J. P. *J. Non-Cryst. Solids* **1992**, 141, 61.
- (31) Birge, N. O.; Nagel, S. R. *Phys. Rev. Lett.* **1985**, 54, 2674.
- (32) Birge, N. O. *Phys. Rev. B* **1986**, 34, 1631.
- (33) Lindsey, C.; Patterson, G. *J. Chem. Phys.* **1980**, 73, 3348.