Frequency-domain study of physical aging in a simple liquid

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We characterize the time dependence of the frequency-dependent dielectric susceptibility of glycerol following quenches to low temperature. For quenches to temperatures not far below the glass-transition temperature, the spectral shape and position during equilibration closely approximate those of equilibrium spectra at higher temperatures. For deeper quenches the correspondence with equilibrium spectra breaks down, and we observe more subtle behavior. Most of the susceptibility's change with time occurs within one *equilibrium* relaxation time after the quench, and our results do not support the presence of a significant ultraslow component to the equilibration of the dielectric response. We find some qualitative agreement between the time dependence of the susceptibility and analogous measurements on spin glasses; however, closer inspection reveals that the liquid fails to reproduce many of the salient features of the spin-glass behavior. [S0163-1829(98)05309-0]

I. INTRODUCTION

A general feature of systems with long relaxation times, such as a supercooled liquid in its glass transition region, is the protracted approach to equilibrium following a temperature (or pressure) change. During this equilibration, which is often termed physical aging, the liquid's bulk properties, such as its volume and enthalpy, vary as the system approaches equilibrium. In addition, the dynamics of the liquid, such as its mechanical or dielectric response, similarly evolve in time.

In an effort to characterize aging in a simple liquid, we have measured the change with time of the frequency-dependent dielectric susceptibility in supercooled glycerol following quenches through its glass-transition temperature, T_g. We have also performed dielectric studies of aging in three other simple liquids: propylene glycol, propylene carbonate, and tricresyl phosphate. (We use the term simple liquid to describe glycerol and these other liquids to distinguish them from polymeric systems. Glycerol is a strongly hydrogen-bonding molecular liquid.) Because our most extensive studies are on glycerol, the results we present here are for this liquid. Our measurements on the other liquids are consistent with these results. Extensive research on aging in polymers[1] has characterized the time dependence of response functions in these systems. However, the vast majority of these studies have been time-domain measurements, and our frequency-domain study on simple liquids complements this approach. (Although we are aware of one short account of a frequency-domain, dielectric study of aging in a polymer,[2] we know of no comprehensive examination of aging in the frequency domain on polymers or simple liquids.)

Recently, aging behavior has played an increasingly important role in efforts to understand the microscopic physics of disordered systems. Aging in spin glasses has been analyzed in an effort to distinguish among the theoretical pictures proposed for these systems.[3] Our measurements of the dielectric response in liquids provide a direct analogy with the magnetic-susceptibility aging studies in spin glasses. We can thus examine if theories proposed for spin glasses have relevance for liquids.

In the case of deeply supercooled liquids, the equilibrium

linear-response dynamics is typically nonexponential, and several experiments[4] have indicated that this broadening results from dynamic heterogeneities. Do these heterogeneous dynamics imply spatially extended, structurally heterogeneous regions in the liquids? Miller and Macphail[5] have suggested that the presence of such extended regions could have consequences in the aging of supercooled liquids. One goal of our study has been to search for evidence in the aging of the dielectric response that might support the existence of extended domains.

This paper is organized as follows. Section II reviews the properties of the dielectric susceptibility of equilibrated supercooled liquids. Section III describes the experimental procedure. Section IV summarizes our results. Specifically, after quenches to temperatures not far below T_g, the shape and position of $\varepsilon''(\nu)$ at different times during aging mimic the equilibrium response at higher temperatures. However, at lower temperatures this scenario breaks down. We compare our results with the aging behavior in spin glasses and find that the aging in simple liquids possesses qualities distinct from those in the spin systems. Finally, in Sec. V we conclude.

II. EQUILIBRIUM SPECTRAL SHAPE

We have measured the dielectric susceptibility $\varepsilon(t_a,\nu) = \varepsilon'(t_a,\nu) + i\varepsilon''(t_a,\nu)$ as a function of frequency ν and aging time t_a. As Fig. 1 illustrates, the imaginary part of the spectrum for glycerol in equilibrium $\varepsilon''_{eq}(\nu) \equiv \varepsilon''(t_a \to \infty, \nu)$ contains a broad, asymmetric peak characteristic of supercooled liquids. The frequency of the peak ν_p for glycerol follows a Vogel-Fulcher law

$$\log_{10}(\nu_p) = \log_{10}(\nu_0) - A/(T-T_0), \qquad (1)$$

with $T_0 \approx 134$ K, $\nu_0 \approx 10^{13}$ Hz, and $A \approx 870$ K. At T_g, $\nu_p \approx 10^{-3}$ Hz, which lies below our lowest measurement frequency of 4×10^{-2} Hz. Therefore, in the aging experiments we probe the evolution with time of the susceptibility above the peak.

A detailed study[6] of the equilibrium response for glycerol and several other liquids near T_g has revealed three power-
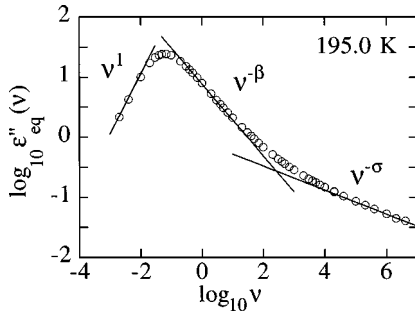
FIG. 1. The equilibrium dielectric spectrum for glycerol, $\varepsilon''_{eq}(\nu) \equiv \varepsilon''(t_a \to \infty, \nu)$, at 195.0 K. The spectrum contains two distinct power-law regions above ν_p.

FIG. 2. ε''_{eq} ($\nu = 100$ Hz) vs temperature (circles) compared with $\varepsilon''(t_a \approx 0, \nu = 100$ Hz) (solid line). The two measurements depart from one another below the glass-transition temperature, $T_g = 190$ K.

law regions: one below ν_p and two above the peak, as indicated in Fig. 1. The exponent of the power law in the highest frequency region $-\sigma$ has a linear temperature dependence near T_g,

$$\sigma = B(T - T_\sigma), \qquad (2)$$

where $T_\sigma \approx T_0$. For glycerol we find $B \approx 0.0039$. The exponent of the power law just above the peak $-\beta$ also changes with temperature to maintain the relation

$$(\sigma+1)/(\beta+1) = 0.72. \qquad (3)$$

This temperature dependence of the spectral shape forms the basis of a recent argument that the static dielectric susceptibility in supercooled liquids diverges at T_0.[6,7] That argument assumes that σ approaches 0 at T_0, as predicted by Eq. (2). One interest in our aging studies has been to determine whether the aging-time dependence of the spectrum can provide information about the equilibrium behavior of σ in the temperature region where measurements on the fully equilibrated liquid are not feasible.

III. EXPERIMENTAL PROCEDURE

We obtained the glycerol (99.5%) from Aldrich Chemical Co. Because the liquid is hygroscopic, we handled it strictly in a dry nitrogen environment. To determine $\varepsilon(t_a, \nu)$, we measured the complex impedance of a capacitor filled with the liquid relative to its impedance when empty. The capacitor consisted of two gold covered parallel plates 2.5 cm in diameter and separated by a 0.025 cm-thick annular Teflon spacer, which held the sample between the plates. We placed the filled capacitor within a heating coil in a copper can, filled the can with a dry nitrogen gas, and submerged it in a liquid-nitrogen dewar. The temperature of the capacitor, measured with a platinum resistance temperature detector, was stable during experiments to better than ± 0.02 K for up to 120 h (the hold time of the dewar). Temperature gradients across the sample were less than 0.05 K.

We measured $\varepsilon(t_a, \nu)$ from $\nu = 4 \times 10^{-2}$ Hz to $\nu = 10^6$ Hz. For measurements up to 10^4 Hz, we placed the reference output of a Stanford 850 digital lock-in amplifier across the capacitor in series with a Keithley 428 current amplifier, and obtained the complex impedance of the circuit by measuring the output of the current amplifier with the lock-in. Above 10^4 Hz, we measured the impedance using a Hewlett Packard 4275A LCR meter.
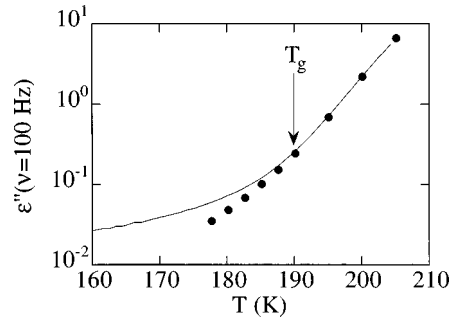
We began each measurement by holding the liquid at 206.2 K for several hours to be sure it was well equilibrated there. (At this temperature, equilibrium relaxation times are less than 0.02 s.) We then rapidly cooled the liquid to a low temperature where we monitored the aging. The cooling rate during the quenches was 1.5 K/min. Figure 2 shows $\varepsilon''(t_a \approx 0, \nu = 100$ Hz) measured during cooling in comparison with the equilibrium values, $\varepsilon''(t_a \to \infty, \nu = 100$ Hz). The value during cooling begins to diverge from the equilibrium value near 190 K. This divergence signifies that structural relaxation times in the liquid have grown larger than the experimental time scale set by the cooling rate and that the liquid has fallen from equilibrium. We equate this temperature with T_g.

During cooling the temperature typically undershot the set point by about 4 K and then steadily increased until the final temperature was reached. The total thermal equilibration took approximately 5000 s. In our analysis we include data taken only after the liquid reaches thermal equilibrium at the final temperature. Because the sample experienced this complicated thermal history before reaching thermal equilibrium, the correct origin for the aging time t_a has some uncertainty; we equate t_a with the time elapsed since the liquid passed through T_g. For most quenches, we monitored aging until $t_a \approx 4 \times 10^5$ s (the hold time of the liquid nitrogen dewar). However, at some temperatures we carefully replenished the liquid nitrogen to track aging to $t_a \approx 2.5 \times 10^6$ s.

IV. TIME DEPENDENCE OF SUSCEPTIBILITY FOLLOWING A QUENCH

We apply two complementary methods for analyzing $\varepsilon(t_a, \nu)$. (1) In Sec. IV A we compare the spectral shape and position at one aging time with those at later times. Essentially, this method attempts to scale the response at different aging times by shifting $\varepsilon(t_a, \nu)$ *horizontally* along the $\log_{10} \nu$ axis. The degree to which such scaling fails indicates how the spectral shape changes with time. The study of physical aging in polymers focuses on the aging-time dependence of response functions and takes primarily this point of view. Viewing the changing spectral shape with aging time also offers a suitable perspective for placing our results in the context of phenomenological models that have been developed to describe aging. (2) In Sec. IV B we consider the aging-time dependence of $\varepsilon(t_a, \nu)$ at a fixed frequency. (That is, we shift the data *vertically* along the $\log_{10} \varepsilon$ axis.)
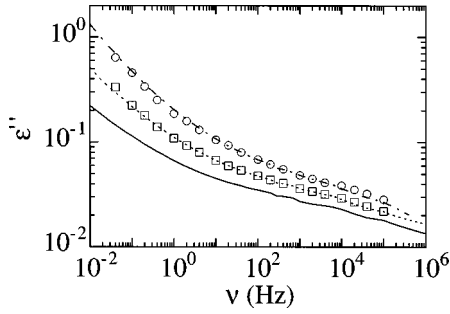
FIG. 3. $\varepsilon''(t_a,\nu)$ vs frequency following a quench from 206.2 to 177.6 K at two different aging times: $t_a = 200$ s (circles) and $t_a = 2 \times 10^4$ s (squares). The lines are equilibrium spectra at three temperatures: 177.6 K (solid), 180.1 K (dotted), and 182.5 K (dot-dashed). The spectrum after 200 s at 177.6 K closely approximates the equilibrium spectrum at 182.5 K. Likewise, the spectrum after the longer aging time of 2×10^4 s closely resembles the equilibrium spectrum at the lower temperature, 180.1 K.

This approach is the method commonly taken in aging studies on spin glasses, and in Sec. IV C we analyze our results in the context of spin-glass models. In Sec. IV D we describe an experiment that looks for "pre-aging" phenomena like those recently found in simulations.

A. Aging-time dependence of the spectral shape

We focus on the imaginary part of the susceptibility $\varepsilon''(t_a,\nu)$, since this term shows a much larger fractional change during aging than does the real part, $\varepsilon'(t_a,\nu)$. Figure 3 shows $\varepsilon''(t_a = 200\text{ s},\nu)$ and $\varepsilon''(t_a = 2 \times 10^4\text{ s},\nu)$ following a quench from 206.2 K to 177.6 K. [We construct the spectrum $t_a = 200$ s by extrapolating $\varepsilon''(t_a,\nu)$ at each ν with Eq. (5) given below.] The lines in the figure are the equilibrium spectra, $\varepsilon''_{eq}(\nu) \equiv \varepsilon''(t_a \rightarrow \infty,\nu)$, measured at 177.6 K (solid), 180.1 K (dotted), and 182.5 K (dot-dashed). As the figure illustrates, the spectral shape and position at different times during aging at 177.6 K closely approximate those of equilibrium spectra at higher temperature. As mentioned above, a detailed study of $\varepsilon''_{eq}(\nu)$ has revealed that the exponents of the two power-law regions above the peak β and σ decrease with decreasing temperature. Therefore, the association of $\varepsilon''(t_a,\nu)$ with $\varepsilon''_{eq}(\nu)$ at different temperatures (with earlier t_a corresponding to higher temperature) implies that during aging the spectral shape is similarly changing with time.

We note that this changing spectral shape with aging time in glycerol contradicts the "time/aging-time superposition principle" often applied to aging in polymers. In his extensive study of aging in polymers, Struik[1] developed this principle, in which the (time-domain) response functions maintain a shape on a log-time scale independent of t_a and shift to longer time (or, equivalently, lower frequency) with aging as t/t_a^μ. Several studies have indicated that time/aging-time superposition is not universally held in polymers. In particular, two recent time-domain dielectric experiments have reported aging-time dependence in the shape of the dielectric response.[8,9] However, neither of these studies associated the shape at different aging times with higher temperature equilibrium shapes as we have done here for the aging in simple liquids.

To illustrate more concretely the aging-time dependence of the spectral shape in glycerol, we display in Fig. 4 the
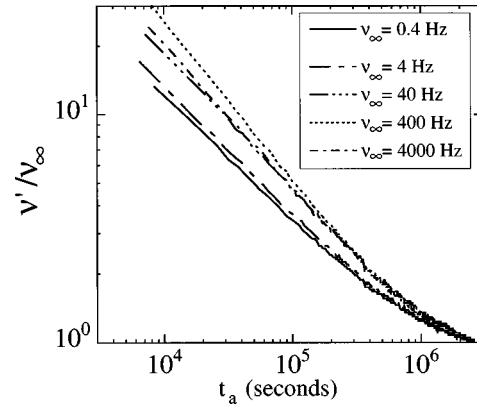

FIG. 4. The ratio of the frequencies $\nu'(t_a)$ and ν_∞ for which $\varepsilon''(t_a,\nu') = \varepsilon''_{eq}(\nu_\infty)$ vs aging time t_a, after a quench to 177.6 K. The different curves are for ν_∞ ranging from 0.4 to 4000 Hz. If the spectral shape were aging-time-independent, these curves would all lie on top of one another. The departure of these curves from one another indicates the degree to which the dielectric response violates time/aging-time superposition.

frequency $\nu'(t_a)$, at which $\varepsilon''(t_a,\nu')$ takes on a particular value after a quench to 177.6 K normalized by the frequency ν_∞, at which $\varepsilon''_{eq}(\nu_\infty)$ at 177.6 K has this same value. Specifically, we plot $\nu'(t_a)/\nu_\infty$ for which

$$\varepsilon''(t_a,\nu') = \varepsilon''_{eq}(\nu_\infty) \tag{4}$$

for ν_∞ ranging from 0.4 to 4000 Hz. [In graphical terms, we are plotting the horizontal shift (on the logarithmic frequency axis) that is necessary to bring $\varepsilon''(t_a,\nu')$ for a given value of t_a on top of the equilibrium curve, $\varepsilon''_{eq}(\nu_\infty)$.] If the spectral shape were aging-time-independent, then the change in $\nu'(t_a)/\nu_\infty$ with t_a would be independent of $\varepsilon''_{eq}(\nu_\infty)$, and these curves would collapse onto a single line. The variation with ν_∞ displayed in Fig. 4 is consistent with the spectral shape mimicking higher temperature equilibrium shapes during aging. For example, the circles in Fig. 5 are $\nu'(t_a)/\nu_\infty$ at $t_a = 2 \times 10^4$ s, and the solid line is ν'/ν_∞ obtained by substituting $\varepsilon''(t_a,\nu')$ in Eq. (4) with $\varepsilon''_{eq}(\nu')$ at 180.1 K. In each case the ratio follows the same trend, illustrating the close association between the spectral shape during aging and equilibrium shapes at higher temperatures.

This effective temperature that the evolving spectral shape assumes during aging bears a close resemblance to the fictive temperature from the phenomenological model Narayanaswamy[10] and Moynihan et al.[11] developed to describe the aging-time dependence of bulk properties in quenched liquids. In this model the fictive temperature, T_F, accounts for the effects of the nonequilibrium structure of the liquid on the equilibration rate of these properties. For example, following a quench through T_g, a liquid's density is smaller than its equilibrium density, and T_F is defined as the temperature at which this nonequilibrium density is the equilibrium value. Although T_F has proven a useful concept in analyzing aging data, a correspondence between T_F and the nonequilibrium state of the liquid is often questioned because, for example, the time dependence one obtains for T_F typically varies with the quantity under observation.[11] However, the behavior of $\varepsilon''(t_a,\nu)$ seems to give physical substance to the notion of a fictive temperature, since this tem-
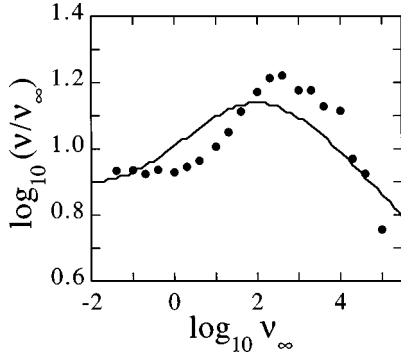
FIG. 5. The ratio of the frequencies $\nu'(t_a = 2 \times 10^4 \text{ s})$ and ν_∞ for which $\varepsilon''(t_a, \nu') = \varepsilon''_{\text{eq}}(\nu_\infty)$ after a quench to 177.6 K as a function of ν_∞. The solid line is the frequency ratio, $\nu_{\infty, T=180.1}$ and $\nu_{\infty, T=177.6}$, necessary to bring the higher temperature equilibrium spectrum at 180.1 K on to the equilibrium spectrum at 177.6 K. The two ratios have very similar frequency dependencies.

perature can be defined not only for a single quantity, which is always possible by definition, but to an entire response function.

While this association between $\varepsilon''(t_a, \nu)$ at different t_a and $\varepsilon''_{\text{eq}}(\nu)$ at different temperatures appears accurate for quenches to temperatures not far below T_g, deviations become increasingly apparent with decreasing temperature. Figure 6 shows $\varepsilon''(t_a = 10^4 \text{ s}, \nu)$ for a series of temperatures ranging from 140.9 K to 177.6 K. The spectra at low temperature in Fig. 6 are not consistent with an equilibrium spectrum at any temperature. For example, at 140.9 K $\varepsilon''(t_a = 10^4 \text{ s}, \nu)$ above 0.4 Hz appears well fit by a single asymptotic power law: $\varepsilon''(t_a = 10^4 \text{ s}, \nu) = D\nu^{-\sigma}$ with $\sigma = 0.10$. This value for σ corresponds through Eq. (2) to an equilibrium temperature near 177 K. However, the small value of D suggests that the spectrum reaches a peak at a frequency orders of magnitude below the equilibrium value, $\nu_p \approx 7 \times 10^{-8}$ Hz, at 177 K.

Thus, after deep quenches the phenomenology becomes more complicated. The spectral shape continues to resemble an equilibrium shape, but its position in frequency is much lower than the equilibrium position corresponding to that shape. Thus, two effective temperatures seem necessary to produce a full description of the response during aging, and with increasing quench depth these temperatures become increasingly separated. The more rapid decrease of the spectral position with quench depth indicates that the mean dielectric
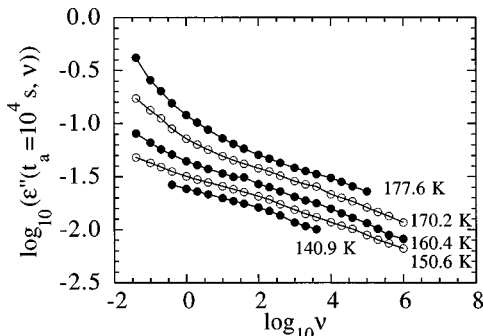

FIG. 6. $\varepsilon''(t_a = 10^4 \text{ s}, \nu)$ for a series of temperatures ranging from 140.9 to 177.6 K. The spectra at low temperature are not consistent with an equilibrium spectrum at any temperature.
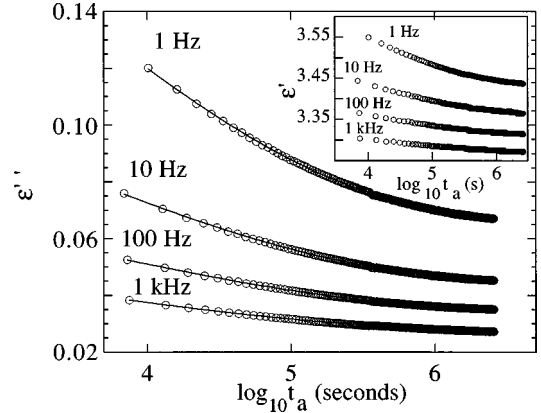

FIG. 7. The change with t_a of $\varepsilon''(t_a, \nu)|_\nu$ at several fixed frequencies for a quench to 177.6 K. The inset shows the real part of the susceptibility, $\varepsilon'(t_a, \nu)$, for the same frequencies. The shape of the decays is typical of the aging-time dependence seen at all temperatures and frequencies. Fits to a stretched exponential function, given by the solid lines, provide a good description of $\varepsilon''(t_a, \nu)$ at fixed ν over the entire range of t_a that we access.

response time is sensitive to the liquid's temperature. The shape of the response, on the other hand, continues to resemble equilibrium shapes for temperatures not far below T_g, and thus depends less strongly on temperature and more on the nonequilibrium structural state created in the liquid by quenching through T_g.

B. Aging-time dependence of the susceptibility at fixed frequency

In addition to tracking the changing spectral shape with aging time, we can also examine the change that the susceptibility at fixed frequency experiences after a quench. Figure 7 shows the change with t_a of $\varepsilon''(t_a, \nu)|_\nu$ at several fixed frequencies for a quench to 177.6 K. The inset to the figure shows the real part of the susceptibility $\varepsilon'(t_a, \nu)$ for the same frequencies. The shape of the decays in Fig. 7 is typical of the aging-time dependence seen at all temperatures and frequencies. In general, the curves are not well fit by a straight line, which would have implied logarithmic relaxation. We find that a stretched exponential function in the aging time provides an excellent description of $\varepsilon''(t_a, \nu)$ at fixed ν over the entire range of t_a that we access:

$$\varepsilon''(t_a, \nu)|_\nu = \Delta\varepsilon''_\nu \exp[-(t_a/\tau)^\beta] + \varepsilon''^{\text{eq}}_\nu. \quad (5)$$

The decay time, τ, follows an Arrhenius temperature dependence, as shown in Fig. 8(a) for $\nu = 1$ Hz. Figure 8(b) shows the temperature dependence of β for $\nu = 1$ Hz. Except at temperatures just below T_g, β maintains a temperature independent value near 0.25. (The slight upward trend in β with decreasing temperature below 179 K is not statistically significant. Below this temperature all of the decay curves at all frequencies are adequately fit assuming a constant value of β near 0.25.)

In a recent study of aging in glycerol by stimulated Brillouin scattering, Miller and MacPhail[5] observed that aging at a temperature continued for many times longer than the equilibrium structural relaxation times measured in the linear-response regime. They described the time dependence of the Brillouin peak shift with a stretched-exponential decay plus
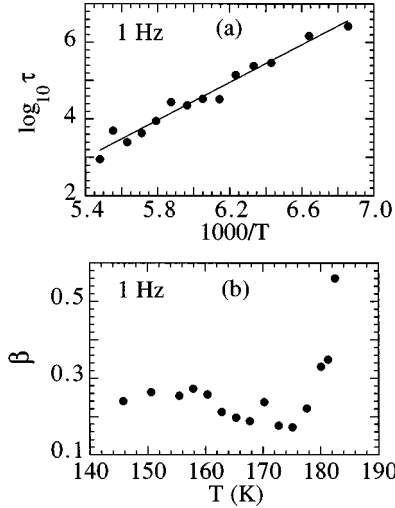
FIG. 8. (a) The decay time τ and (b) β from stretched exponential fits to $\varepsilon''(t_a, \nu = 1\,\text{Hz})$ at various temperatures. The Arrhenius temperature dependence of τ is typical of the behavior at all frequencies. Below 179 K, β is temperature-independent.

an additional exponential decay to account for an ultraslow component in the aging. Introducing such an additional term to Eq. (5) gives

$$\varepsilon''(t_a, \nu)\big|_\nu = \Delta\varepsilon''_u \exp(-t_a/\tau_u)$$
$$+ \Delta\varepsilon''_s \exp[-(t_a/\tau_s)^\beta] + \varepsilon''^{\text{eq}}_\nu. \qquad (6)$$

Miller and MacPhail noted that the existence of such a long-time component is consistent with models for the nonexponential relaxation in supercooled liquids that predict spatially extended dynamically heterogeneous regions in the liquids. We have searched for the presence of a long-time component in the decays of $\varepsilon''(t_a, \nu)\big|_\nu$ at temperatures for which we are able to monitor the aging to what we believe is equilibrium. Figure 9 shows $\varepsilon''(t_a, \nu = 200\,\text{Hz})$ after quenches to 180.1 and 182.5 K with t_a scaled by τ_{eq} for each temperature. (We use $\tau_{\text{eq}} = 8.1 \times 10^3$ s at 182.5 K and $\tau_{\text{eq}} = 6.3 \times 10^4$ s at 180.1 K. These values for the equilibrium relaxation times result from setting $\tau_{\text{eq}} = 1/2\pi\nu_p$, where we obtain ν_p from extrapolations of higher temperature data through Eq. (1). In supercooled liquids the dielectric relaxation time, defined in this way, closely tracks with temperature the structural relaxation times extracted from frequency-dependent specific heat and shear viscosity measurements.[12]) As Fig. 9 illustrates, all of the measurable aging occurs at $t_a/\tau_{\text{eq}} < 10$, and beyond this point the susceptibility is independent of time. (We estimate the precision of the experiments would allow us to distinguish changes in ε'' greater than 1% on the time scale of these measurements.) The inset of Fig. 9 shows the region at large t_a on an expanded scale to emphasize this point. While this time scale for equilibration appears roughly consistent with that observed by Miller and MacPhail, our data do not support the addition of an ultraslow component in the description of the decay. Attempting to fit $\varepsilon''(t_a, \nu)\big|_\nu$ with Eq. (6), we find $\Delta\varepsilon''_u$, the strength of an ultraslow component, averages less than $0.04\Delta\varepsilon''_s$ at both 180.1 and 182.5 K. (To reduce the number of free parameters in these fits, we set
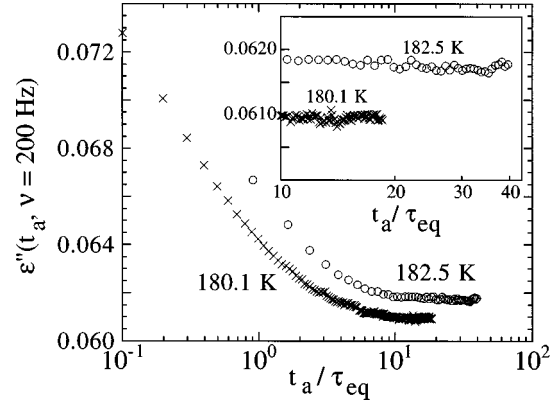

FIG. 9. $\varepsilon''(t_a, \nu = 200\,\text{Hz})$ after quenches to 180.1 and 182.5 K vs t_a/τ_{eq} for each temperature. The data for 180.1 K have been offset by 0.017 for clarity. All of the measurable aging occurs at $t_a/\tau_{\text{eq}} < 10$, and beyond this point the susceptibility is independent of time. Inset shows the region at large t_a on an expanded scale.

$\tau_u = 35\tau_s$, the ratio Miller and MacPhail obtained.) Constraining $\Delta\varepsilon''_u$ to a larger value (for example, $0.5\Delta\varepsilon''_s$ as Miller and MacPhail obtained) gives markedly worse fits than Eq. (5), with the same number of free parameters. The fit results from Eq. (5) give averages for $\exp[-(\tau_{\text{eq}}/\tau)^\beta]$ of 0.25 at 182.5 K, 0.10 at 180.1 K, and 0.03 at 177.6 K. (Miller and Macphail, on the other hand, obtain a value for $\exp[-(\tau_{\text{eq}}/\tau)^\beta]$ near 0.35 at 179.8 K after quenching from above 192 K.) These numbers suggest that the significant portion of the aging, as measured by dielectric response, occurs within one τ_{eq} of the quench. Therefore, from this analysis we conclude that our results are not consistent with an ultraslow component to the aging. This observation, that the linear response behavior of glycerol reaches equilibrium following a quench faster than does the sound velocity (which depends directly on density), has been noted for an epoxy glass by Santore and co-workers[13] who simultaneously measured the mechanical response and density during aging.

Finally we note that the shapes of $\varepsilon''(t_a, \nu)\big|_\nu$ at a given temperature have a slight frequency dependence. This dependence appears as an increase in τ with ν when β in Eq. (5) is held fixed, such as in Fig. 10(a). Alternatively, fixing τ leads to a decrease in β with increasing ν, as in Fig. 10(b). (Allowing both parameters to vary simultaneously introduces scatter that obscures these trends.)

C. Comparison with aging in spin glasses

1. Scaling the susceptibility

Analysis of aging in spin glasses has provided insights into the microscopic physics of these systems, and one motivation for our study has been to compare the behavior we observe in simple liquids with aging in spin glasses. A number of studies on spin glasses have monitored the aging-time dependence of the frequency-dependent magnetic susceptibility, $\chi(t_a, \nu)$, following temperature quenches. The time dependence of $\varepsilon''(t_a, \nu)$ at fixed ν, such as shown in Fig. 7, appears, at least superficially, very similar to that observed for $\chi''(t_a, \nu)$ at fixed ν.[14,15] Indeed, over a limited range of time the behavior of $\varepsilon''(t_a, \nu)$ closely resembles both the
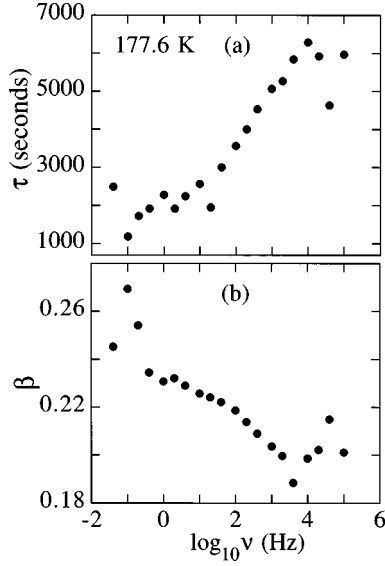
FIG. 10. (a) τ vs ν for the decays at 177.6 K (such as in Fig. 7) when β in the stretched-exponential form [Eq. (5)] is held fixed. (b) β vs ν for the same decays when τ is held fixed. These results indicate that the shape of the decay has a slight frequency dependence.
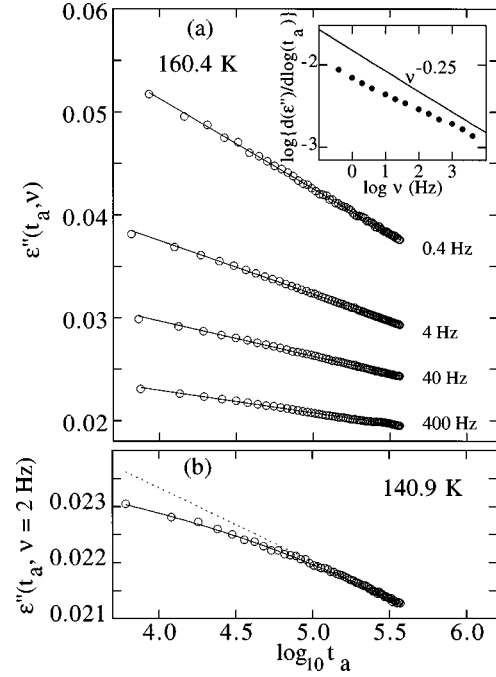

FIG. 11. (a) $\varepsilon''(t_a,\nu)$ for several frequencies at 160.4 K vs $\log_{10} t_a$. The inset shows the rate of decay, $d(\varepsilon'')/d(\log_{10} t_a)$, in the range $0.1\tau < t_a < 10\tau$. The frequency dependence of the decay rate is similar to the $\nu^{-0.25}$ dependence reported for the decay of χ'' in a spin glass (Ref. 14). However, we observe deviations from this logarithmic decay both for $t_a \ll \tau$ and $t_a \gg \tau$. (b) $\varepsilon''(t_a,\nu=2\,\text{Hz})$ at 140.9 K on a $\log_{10} t_a$ scale. (At this temperature $\tau > 10^8$ s.) The dashed line in the figure is a guide to highlight the deviations from logarithmic behavior. The solid line through the data is a fit to Eq. (5).

$\log_{10} t_a$ decay[14] and power-law decay[15] reported for $\chi''(t_a,\nu)$ in spin glasses. [For $\beta \approx 0.25$, Eq. (5) is essentially indistinguishable from a $\log_{10} t_a$ decay for $0.1\tau < t_a < 10\tau$.] However, by quenching to very low temperatures, so that we can access the aging at relatively early times, we observe deviations from log decay and power-law decay, consistent with Eq. (5).

As an illustration of the similarity between the liquid and spin-glass aging behaviors, Fig. 11(a) shows $\varepsilon''(t_a,\nu)$ for several frequencies at 160.4 K on a $\log_{10} t_a$ scale. The rate of decay, $d(\chi'')/d(\log_{10} t_a)$, for a spin glass was reported to vary as $\nu^{-0.25}$.[14] Fitting within the range $0.1\tau < t_a < 10\tau$, we find a similar frequency dependence for the decay of ε'', as the inset to Fig. 11(a) illustrates. [In terms of Eq. (5), $d(\varepsilon'')/d(\log_{10} t_a) = -\Delta\varepsilon''_\nu \beta/(e \log_{10} e)$ at $t_a = \tau$. Thus, this frequency dependence simply reflects the frequency dependence of $\Delta\varepsilon''_\nu$ and β.] We stress again, however, that we observe deviations from logarithmic decay, consistent with Eq. (5), both for $t_a \ll \tau$ and $t_a \gg \tau$. The deviations at large t_a are apparent in Fig. 7. To illustrate the deviations at small t_a, we show in Fig. 11(b) $\varepsilon''(t_a,\nu=2\,\text{Hz})$ at 140.9 K on a $\log_{10} t_a$ scale (At this temperature $\tau > 10^8$ s.) The dashed line in the figure is a guide to highlight the deviations from logarithmic behavior. The solid line through the data is a fit to Eq. (5).

To illustrate the range of applicability of a power-law description to $\varepsilon''(t_a,\nu)|_\nu$, we show in Fig. 12 $\varepsilon''(t_a,\nu=2\,\text{Hz})$ on a log-log scale for (a) $T=140.9$ K, (b) $T=172.7$ K, and (c) $T=180.1$ K. At these low, intermediate, and high temperatures we monitor the aging at relatively early, intermediate and late times, respectively. The solid lines in Figs 12(a) and 12(c), which are fits to a stretched exponential decay [Eq. (5)], again demonstrate its good agreement to the data throughout the aging times we access. The dotted lines in Figs 12(b) and 12(c) are fits to a power-law decay:

$$\varepsilon''(t_a,\nu)|_\nu = A_\nu t_a^{-\alpha} + \varepsilon_\nu''^{\text{eq}}. \qquad (7)$$

As Fig. 12(b) illustrates, the decay of $\varepsilon''(t_a,\nu)|_\nu$ is consistent with a power law over an extended period during aging. Equation (7) also provides a fair description of the final approach to equilibrium, as Fig. 12(c) illustrates. (Fits to the stretched-exponential form, which benefits from one additional free parameter, are superior in this region.) However, clear deviations from a power-law decay are apparent during the early period of aging accessed at low temperature, as in Fig. 12(a). At these aging times, the rate of decay of $\varepsilon''(t_a,\nu)|_\nu$ on a log-log scale increases with aging time, in contrast to the behavior predicted by Eq. (7).

We have attempted to scale $\varepsilon''(t_a,\nu)$ at different frequencies following a procedure suggested for $\chi''(t_a,\nu)$ of spin glasses[3] in which the difference in susceptibility from its equilibrium value is scaled against νt_a. (We note that in the spin glasses the equilibrium spectra are not measured, and consequently some freedom exists for choosing the subtracted values.) Figure 13(a) which displays an effort to scale the data at 180.1 K, demonstrates that the scaling does not work for glycerol. Figure 13(b) shows the νt_a scaling applied to $\varepsilon''(t_a,\nu)$ at a lower temperature, 162.8 K. Because we do not know $\varepsilon''_{\text{eq}}(\nu)$ at this temperature, we have chosen offsets, $C(\nu)$, for each frequency to optimize the scaling. However, even introducing this free parameter fails to pro-
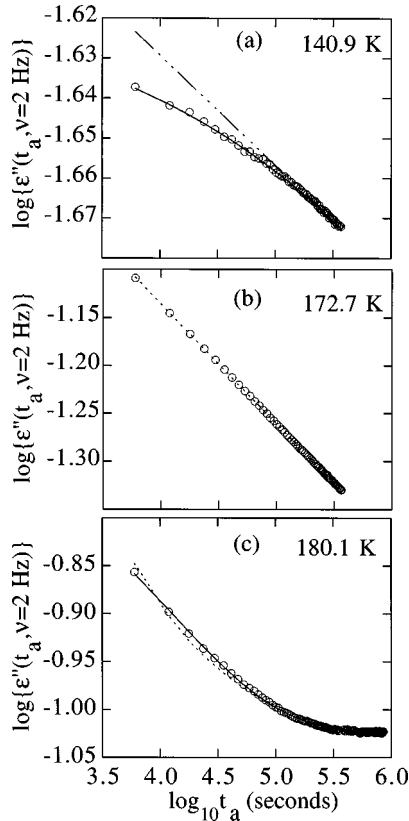
FIG. 12. $\varepsilon''(t_a, \nu = 2$ Hz$)$ on a log-log scale for quenches to (a) $T = 140.9$ K, (b) $T = 172.7$ K, and (c) $T = 180.1$ K. At these low, intermediate, and high temperatures we monitor the aging at relatively early, intermediate and late times, respectively. The solid lines in (a) and (c) are fits to a stretched exponential decay. The dotted lines in (b) and (c) are fits to a power-law decay. The dash-dotted line in (a) is a straight line "guide to the eye."

FIG. 13. The difference in susceptibility from its equilibrium value, $\varepsilon''(t_a, \nu) - \varepsilon''_{eq}(\nu)$, plotted vs νt_a for (a) 180.1 K and (b) 162.8 K. For 162.8 K $\varepsilon''_{eq}(\nu)$ is not known; therefore, we choose values, $C(\nu)$, to optimize the overlap between frequencies. This scaling procedure, proposed for spin glasses, does not work for glycerol.

vide good scaling. (At this temperature, a $\log_{10} t_a$ dependence approximates the aging well for the entire time we record the decay. Since the slope of $\varepsilon''(t_a, \nu)$ vs $\log_{10} t_a$ decreases with increasing frequency [see the inset to Fig. 11(a)], we should not expect the data at this temperature to obey νt_a scaling.) Successful νt_a scaling of the transient response implies that, at sufficiently high frequency, the susceptibility reaches its equilibrium value arbitrarily rapidly. This scenario appears valid for spin glasses for which $\chi''(t_a, \nu)$ reaches equilibrium quickly at high frequency.[3,14] However, in glycerol we observe changes with aging time in $\varepsilon''(t_a, \nu)$ up to $\nu = 10^6$ Hz (our highest frequency) throughout the measurement time ($t_a > 4 \times 10^5$ s). From these observations we conclude that, in spite of the similarities highlighted by Figs. 11 and 12, important qualitative differences exist between aging in liquids and in spin glasses and, in particular, that νt_a scaling for the transient portion of the susceptibility is not appropriate for the aging spectra in liquids.

2. Temperature jumps during aging

Many of the insights in the study of spin glasses have come from monitoring the response of $\chi''(t_a, \nu)$ during aging to temperature changes.[3,16] We have attempted the same type of experiments on glycerol to compare its behavior with that of the spin glasses. Figure 14 shows the result of aging
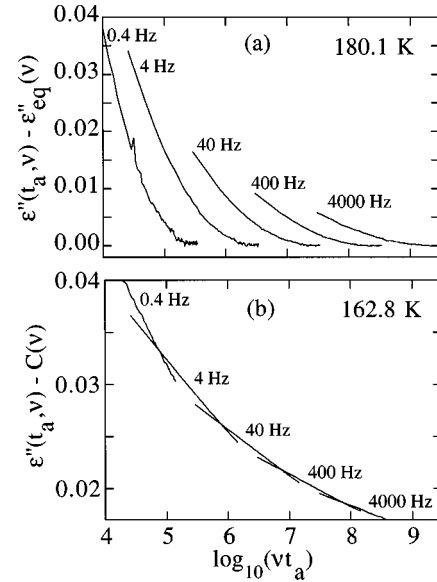
the liquid at 177.6 K for two days, decreasing the temperature to 170.2 K for two days ($\Delta T = -7.4$), and then returning the temperature to 177.6 K. (Figure 14 displays $\varepsilon''(t_a, \nu = 2$ Hz$)$. However, the features are independent of frequency.) The behavior of the liquid in these experiments shows important qualitative differences with that observed for the spin glasses. When the temperature of an aging spin glass is dropped, the susceptibility typically jumps suddenly to a large value and begins a rapid decay, as if the aging process were being restarted. This dramatic behavior constrasts with the drop in susceptibility and slow decay shown at 170.2 K in Fig. 14, and for no value of ΔT have we found such a "restart of aging" in the susceptibility of the liquid. (We have performed six such measurements all with an initial temperature of 177.6 K and with $\Delta T = -2.5$, -4.9, -7.4, -12.3, -17.2, and -27.0 K.)

Upon returning to the initial temperature, the liquid, like the spin glasses, has aged at the lower temperature less than it would have if the temperature had not been lowered, and one might attempt to define an effective time, t_{eff}, to characterize the degree of aging experienced at the lower temperature, as is done for the spin glasses.[16] However, in the liquid the determination of t_{eff} is complicated by the shape of $\varepsilon''(t_a, \nu)$ with aging time following the return to the initial temperature. For sufficiently small ΔT, $\varepsilon''(t_a, \nu)$ increases for a period immediately following the return to the initial temperature before resuming its decrease, as the inset of Fig. 14 illustrates. This increase appears to be an example of the "memory effect" that one observes for a quenched liquid's bulk properties in similar temperature jump experiments.[11] (A phenomenological explanation of this effect was a principal motivation for the development of the Narayanaswamy-Moynihan model.) Therefore, for these studies of temperature jumps, we conclude that the salient features revealing the underlying physics of spin glasses are not reproduced with the liquids.
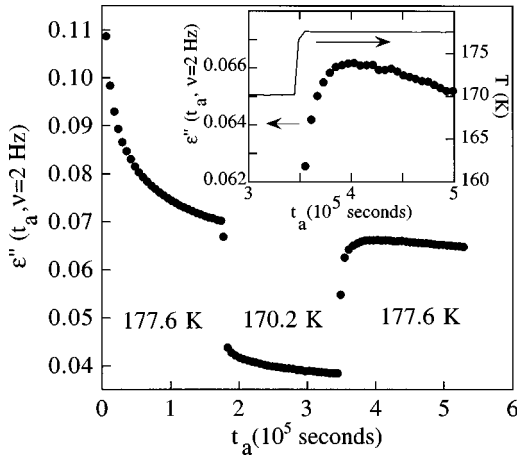
FIG. 14. $\varepsilon''(t_a, \nu = 2 \text{ Hz})$ vs t_a during a measurement in which the temperature was held at 177.6 K for two days, decreased to 170.2 K for two days ($\Delta T = -7.4$), and then returned to 177.6 K. The behavior of the liquid in these experiments shows important qualitative differences with that observed for the spin glasses. The inset shows that, for sufficiently small ΔT, $\varepsilon''(t_a, \nu)$ demonstrates the ''memory effect,'' increasing for a period immediately following its return to the initial temperature before resuming its decrease.

D. Quenches from low initial temperatures

In a recent simulation study of aging in a Lennard-Jones liquid, Kob and Barrat[17] analyzed the dependence on the initial temperature of the aging behavior following a quench. Monitoring the changes with t_a of the self-intermediate scattering function, they observed a period at early t_a in which the scattering function showed no change. Aging commenced only as t_a approached the equilibrium relaxation time at the *initial* temperature. They explained this ''pre-aging'' period with the physically appealing idea that the liquid requires on the order of one relaxation time to realize that the quench has created a nonequilibrium condition and to respond structurally.

Following the quench procedure that we describe in Sec. III, we are not able to access this pre-aging regime. For these quenches, T_g, the temperature at which the sample falls from equilibrium, is effectively the initial temperature, and equilibrium relaxation times at T_g are approximately 100 s, much shorter than the 5000 s the experiment requires for thermal equilibration. Therefore, to search for this pre-aging regime, we have performed a quench to 160.4 K after equilibrating the sample at 180.1 K, where the equilibrium relaxation time is 6.3×10^4 s. (We held the sample at 180.1 K for 14 days before the quench.) Figure 15 shows the resulting decay, $\varepsilon''(t_a, \nu = 2 \text{ Hz})$. In contrast to the simulation, we observe aging at our earliest measurement times, which are approximately one tenth of the equilibrium relaxation time of the initial temperature. No change in the decay rate or other feature appears as t_a passes through τ_{eq} (180.1 K).

The behavior we observe is qualitatively identical to that seen with the other quench procedure (i.e., quenching from above T_g), and Eq. (5) accurately describes $\varepsilon''(t_a, \nu)$ at fixed ν. However, the magnitude and time scale of the decays of $\varepsilon''(t_a, \nu)$ at fixed ν are different. Fits to Eq. (5) give $\tau \approx 7 \times 10^5$ s for this quench from 180.1 K (averaging over 0.4 to 4000 Hz), while its value following a quench from 206.2 K through T_g to this temperature is $\tau \approx 1 \times 10^5$ s. Also, $\Delta \varepsilon_\nu''$ is
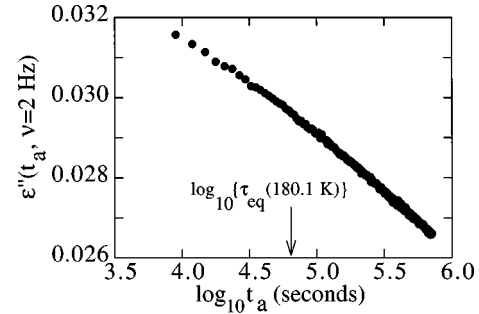

FIG. 15. $\varepsilon''(t_a, \nu = 2 \text{ Hz})$ after a quench from 180.1 to 160.4 K. Aging has commenced before our earliest measurement times, which are approximately one tenth of the equilibrium relaxation time of the initial temperature. We observe no pre-aging effects [i.e., changes in the decay rate or other features as t_a passes through $\tau_{\text{eq}}(T = 180.1 \text{ K})$].

approximately a factor of two smaller, independent of frequency (between 0.4 and 4000 Hz), after the quench from 180.1 K than it is after a quench from the higher temperature.

V. CONCLUSIONS

In this frequency domain study of aging in a simple liquid we have stressed comparisons with other techniques which monitor equilibration in liquids as well as with aging behavior in spin glasses. These comparisons have not only provided information about the nonequilibrium dynamics but have also touched on the equilibrium properties of deeply supercooled simple liquids. In particular, the absence in the dielectric response of a significant ultraslow component to the aging, such as that seen with stimulated Brillouin scattering, places constraints on the source of this component since it does not appear to couple strongly to the dielectric susceptibility. Also, our effort to make detailed comparisons between aging in liquids and that in spin glasses has highlighted both the similarities between their behaviors as well as important differences. The aging behavior near T_g seems to fit well within the phenomenological framework of the Narayanaswamy-Moynihan model. Indeed, we see direct physical manifestation of an effective temperature, like the fictive temperature in this model, in the aging-time dependence of the spectral shape. However, the failure of this analysis when extended to results from deeper quenches may indicate its limitations. At these temperatures two effective temperatures seem necessary to characterize the out-of-equilibrium response, one describing the spectral shape and a lower one describing its position. An understanding of this contrasting dependence on quench depth, in particular the relative insensitivity of the initial spectral shape to quench depth, should provide insight not only to the mechanisms that drive aging, but also to the nature of the spectral broadening in equilibrated supercooled liquids.

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