Memory in an aging molecular glass

H. Yardimci and R. L. Leheny
Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, USA
(Dated: March 22, 2022)

The dielectric susceptibility of the molecular liquid sorbitol below its calorimetric glass transition displays memory strikingly similar to that of a variety of glassy materials. During a temporary stop in cooling, the susceptibility changes with time, and upon reheating the susceptibility retraces these changes. To investigate the out-of-equilibrium state of the liquid as it displays this memory, the heating stage of this cycle is interrupted and the subsequent aging characterized. At temperatures above that of the original cooling stop, the liquid enters a state on heating with an effective age that is proportional to the duration of the stop, while at lower temperatures no effective age can be assigned and subtler behavior emerges. These results, which reveal differences with memory displayed by spin glasses, are discussed in the context of the liquid’s energy landscape.

PACS numbers: 05.70.Ln, 64.70.Pf, 77.22.-d

For many condensed matter systems with disorder, a failure to achieve equilibrium can dominate behavior, and understanding the out-of-equilibrium states becomes crucial to their accurate description. During the protracted equilibration of such systems, dynamic correlation functions and response functions are dependent on time and thermal history. This behavior, known as aging, appears in a broad variety of disordered materials including polymers, spin glasses, molecular glasses, gels, and disordered ferroelectrics. The widespread occurrence of aging has led to theoretical explanations that attempt to account for the phenomenon as a general consequence of disorder and has further motivated work into how one might generalize concepts of equilibrium statistical mechanics, such as the fluctuation-dissipation theorem, to the aging “state.” In addition, specific features of aging, particularly in spin glasses, have been interpreted as providing insight into the underlying equilibrium physics of disordered systems.

An intriguing property of many aging systems is the memory of their thermal histories that their bulk thermodynamic properties and response functions display. In this paper, we describe dielectric susceptibility experiments that probe memory in the molecular liquid sorbitol at temperatures below its calorimetric glass transition. These measurements follow an experimental procedure, originally developed for spin glasses and molecular glasses and for the aging “state.” In addition, specific features of aging, particularly in spin glasses, have been interpreted as providing insight into the underlying equilibrium physics of disordered systems.

As explained below, these measurements elucidate the significance of memory in sorbitol and help to identify important differences between the out-of-equilibrium states of structural glasses and spin glasses.

Following the protocol established in Ref. 13, we begin each measurement with sorbitol at T = 276 K, well above the calorimetric glass transition, Tg = 268 K. To create a reference measurement, we cool the liquid at a fixed rate of 0.13 K/minute to 160 K and then heat back to 276 K at the same rate. Figure 1(a) shows the resulting values of the imaginary part of the dielectric susceptibility, ϵ”(ν), at ν = 0.79 Hz as a function of temperature. The hysteresis between cooling and reheating indicates that the system ages during the time spent below Tg. As previous studies of supercooled liquids have demonstrated, ϵ”(ν) at fixed ν (above the peak frequency for the alpha relaxation) decreases with time during aging, consistent with the hysteresis in Fig. 1(a). The broad peak in ϵ”(0.79 Hz) centered near 190 K is a Johari-Goldstein beta relaxation. The aging of this beta peak tracks that of the primary alpha relaxation; details of this behavior will be provided elsewhere.

To characterize the memory, the cooling and reheating is repeated except that the cooling is temporarily stopped at an intermediate temperature, Tstop. Fig. 1(b) displays values of ϵ”(0.79 Hz) versus temperature for a measurement that includes a temporary stop in the cooling for tstop = 12 hours at Tstop = 230 K. The solid lines in the figure are the results without the stop taken from Fig. 1(a). To highlight the effect of a stop, the ratio of the susceptibility measured on cooling with a stop, denoted ϵ”stop, to that without a stop, denoted ϵ”ref, is plotted in Fig. 2(a). Susceptibility ratios from measurements performed with stops at Tstop = 230 K, 215 K, and 200 K for 12 hours are plotted. For T > Tstop, ϵ”stop/ϵ”ref = 1, as expected. The drop in the ratio at Tstop represents the aging that occurs during the stop. Upon further cooling ϵ”stop/ϵ”ref returns to a value near one, suggesting that the out-of-equilibrium state becomes increasingly affected by the aging during the stop as the temperature deviates further from Tstop; that is, suggest-
ing that the liquid “rejuvenates”. Fig. 2(b) shows the ratio of susceptibilities on reheating with and without the previous stops on cooling. Much like the cooling ratio, the heating ratio goes through a minimum at a temperature very close to $T_{stop}$ before returning to one at higher temperatures. This clear duplication, or memory, of the minimum near $T_{stop}$ suggests that the out-of-equilibrium state of the liquid at temperatures in the vicinity of $T_{stop}$ remains sensitive to the previous aging, while at temperatures away from $T_{stop}$, the state remains indifferent to the aging. Longer waiting times at $T_{stop}$ increase the depth of the minimum, leaving its position in temperature unchanged.

As mentioned above, these results for sorbitol, a molecular liquid, appear strikingly similar to those observed in other aging systems [13, 14, 15], suggesting common underlying mechanisms. A central feature of all these memory studies is that the values of susceptibility at temper-atures away from $T_{stop}$ rapidly approach each other regardless of the aging that occurs during the stop. However, as first demonstrated by Kovacs [17], measured values of thermodynamic quantities for aging materials with different thermal histories can coincide even while they are in very different out-of-equilibrium states. Therefore, to investigate the significance of the memory effect in sorbitol, we have determined how the liquid ages when the subsequent reheating is interrupted following the cooling stop. These aging measurements provide a method to characterize the out-of-equilibrium state of the liquid as it retraces the ratio minimum in Fig. 2(b). Significantly, we find that the behavior observed in these measurements is sensitive to whether the liquid is reheated to a temperature that is greater or less than $T_{stop}$.

Figure 3(a) shows a representative set of results for the case when the heating is interrupted at a temperature $T > T_{stop}$. The figure displays $\varepsilon''(0.79 \text{ Hz})$ as a function of aging time, $t_a$, after heating to $T = 220 \text{ K}$ following cooling stops at $T_{stop} = 215 \text{ K}$ of various durations. The behavior of the susceptibility after the heating is inter-
The inset of Fig. 3(b) shows the ratios $t_{\text{shift}}/t_{\text{stop}}$ used to collapse aging curves corresponding to different $t_{\text{stop}}$ as a function of temperature for $T \geq T_{\text{stop}}$, where $T_{\text{stop}} = 215$ K. The temperature dependence displayed by $t_{\text{shift}}/t_{\text{stop}}$ is fully consistent with aging as a thermally activated process within a fixed (i.e., temperature independent) energy landscape. Within such a picture $t_{\text{shift}}/t_{\text{stop}}$ is expected to vary with temperature as

$$\log_e(t_{\text{shift}}/t_{\text{stop}}) = (T_{\text{stop}}/T - 1)\log_e(t_{\text{stop}}/\tau_0)$$

(1)

where $\tau_0$ is a microscopic time scale $\tau_0^{[8]}$. The results of a fit to Eq. (1), shown with the dashed line in the inset, give $\tau_0 \sim 10^{-14}$ s, a physically plausible time scale. Expressed another way, for $t_{\text{stop}} = 86400$ s and $\tau_0$ constrained to the realistic value $\tau_0 = 10^{-13}$ s, Eq. (1) predicts $t_{\text{shift}} = 34000$ s for $T = 220$ K, 9700 s for $T = 227$ K, and 4200 s for $T = 232$ K, which compare closely with the measured values of 46000 s, 10000 s and 4000 s, respectively. We emphasize that this success of activated scaling for a molecular glass contrasts strongly with the behavior of Heisenberg spin glasses, where the “superactivated” nature of the aging is well documented $\tau_0^{[9]}$. This differing sensitivity to temperature in the aging of spin glasses and structural glasses may also be reflected in the contrasting widths in temperature over which the memory effects occur. For example, the deviations, $\epsilon''(0.79$ Hz, $t_{\text{stop}}$) for these measurements with the time axis shifted by $t_{\text{shift}}$ to collapse the results onto a single curve. The inset shows the ratio $t_{\text{shift}}/t_{\text{stop}}$ leading to such collapse of aging curves as a function of inverse temperature for $T > T_{\text{stop}}$, where $T_{\text{stop}} = 215$ K.

![Figure 3](image-url)
Also, if one were to impose a $t_{shift}$ to match $\varepsilon''(0.79 \text{ Hz}, t_a = 0)$ following a cooling stop with the corresponding value without a stop, one would require $t_{shift} >> t_{stop}$.

While the scaling through $t_{shift}$ fails for $T < T_{stop}$, the low temperature aging curves, $\varepsilon''(0.79 \text{ Hz}, t_a)$, can be superposed by introducing additive constants, $\varepsilon_{shift}''$, that shift the curves vertically, as shown in Fig. 4(b) [21]. This scaling through $\varepsilon_{shift}''$ at $T < T_{stop}$ indicates that the aging rate, $d\varepsilon''/dt_a$, is independent of the stopping. Recent simulation studies have shown that aging in structural glasses occurs through a process of hopping among local minima with progressively lower energy within the potential energy landscape of the liquid [21, 22, 23]. Within such a picture, the failure of the scaling through $t_{shift}$ at $T < T_{stop}$ indicates that the aging at $T_{stop}$ directs the system to a location on the landscape after cooling to low temperature that it would never have visited had it been cooled directly to the low temperature and allowed to age (in contrast to when the temperature is raised back to $T > T_{stop}$). However, the structure of the energy landscape must be such that the subsequent aging at low temperature is independent of the system’s location on the landscape and dependent only on the system’s temperature.

In conclusion, by characterizing the aging of the molecular glass sorbitol following interruptions of memory experiments, we have illuminated the out-of-equilibrium state of the system as it displays memory. We find that the nature of the state depends crucially on whether the glass is at a temperature greater or less than $T_{stop}$. This distinction, exemplified by the success of different scaling procedures in Figs. 3(b) and 4(b), points to an interesting evolution of the system. Specifically, when the glass is reheated following a cooling that includes a stop, it goes from a state at low temperature unlike any that it would reach without the stop to a state at high temperature that has only an increased effective age due to the stop. Further studies, particularly those that focus on the crossover between high and low temperature scaling behaviors, would help clarify the significance of these findings. While a smooth crossover between the two behaviors seems likely, its details and its position in temperature could be informative. In addition, we note that for sorbitol $\varepsilon''(0.79 \text{ Hz})$ at the chosen values of $T_{stop}$ has a larger contribution from the beta relaxation at $T < T_{stop}$ than it does at $T > T_{stop}$. While the strong similarity between memory curves for sorbitol and other glassy materials suggests that the beta relaxation is not playing a significant role, measurements on other molecular liquids without such a pronounced beta peak would help clarify its impact on the observed behavior. Finally, we note that simulations of structural glasses, which have recently placed aging in the context of energy landscape features, could further illuminate the significance of the evolution in scaling that occurs between $T < T_{stop}$ and $T > T_{stop}$. In particular, simulation studies that include more complicated thermal histories for the glass, such as those imposed experimentally in this work, could make concrete the features of the energy landscape suggested by these measurements.

We thank J.-P. Bouchaud for helpful discussions. This work was supported by the National Science Foundation under CAREER Award No. DMR-0134377.

[1] STRUIK L. C. E., Physical Aging in Amorphous Polymers and Other Materials (Elsevier, Amsterdam, 1978).

[2] MATSUOKA S., Relaxation Phenomena in Polymers (Hanser, New York, 1992).
[3] VINCENT E., HAMMANN J., OCIO M., BOUCHAUD J.-P. and CUGLIANDOLO L. F., in *Complex Behavior of Glassy Systems*, edited by M. RUBI and C. PEREZ-VICENDE (Springer-Verlag, New York) 1997.

[4] NORDBLAD P., in *Dynamical properties of unconventional magnetic systems*, edited by A. T. SKJELTORP and D. SHERRINGTON (Kluwer, Boston) 1998.

[5] LEHENY R. L. and NAGEL S. R., *Phys. Rev. B*, **57** (2001) 5154.

[6] CIPELLETTI L., MANLEY S., BALL R. C. and WEITZ D. A., *Phys. Rev. Lett.*, **84** (2000) 2275.

[7] KNAEBEL A., BELLOUR M., MUNCH J. P., VIASNOFF V., LEQUEUX F. and HARDEN J. L., *Europhys. Lett.*, **52** (2000) 73.

[8] ALBERICI F., DOUSSINEAU P. and LEVELUT A., *J. Phys. I France*, **7** (1997) 329.

[9] COLL A. E. V., CHAO L. K., WEISSMAN M. B. and VIEHLAND D. D., *Phys. Rev. Lett.*, **85** (2000) 3033.

[10] BOUCHAUD J.-P., in *Soft and Fragile Matter: Nonequilibrium Dynamics, Metastability and Flow*, edited by M. E. CATES and M. R. EVANS, (IOP, Bristol) 2000.

[11] CUGLIANDOLO L. F., KURCHAN J. and PELITI L., *Phys. Rev. E*, **55** (1997) 3898.

[12] GRIGERA T. S. and ISRAELOFF N. E., *Phys. Rev. Lett.*, **83** (1999) 5038.

[13] JONASON K., VINCENT E., HAMMANN J., BOUCHAUD J.P. and NORDBLAD P., *Phys. Rev. Lett.*, **81** (1998) 3243.

[14] BELLON L., CILIBERTO S., LAROCHE C., *Europhys. Lett.*, **51** (2000) 551.

[15] DOUSSINEAU P., De LACERDA-ARÔSO T., and LEVELUT A., *Europhys. Lett.*, **46** (1999) 401.

[16] YARDIMCI H. and LEHENY R. L., in preparation.

[17] KOVACS A. J., *J. Polym. Sci.*, **30** (1958) 131.

[18] REFREGIER P., VINCENT E., HAMMANN J. and OCIO M., *J. Physique*, **48** (1987) 1533.

[19] BELLON L., CILIBERTO S., LAROCHE C., *Eur. Phys. J. B*, **25** (2002) 223.

[20] Given the relative values of $\varepsilon"(0.79 \text{ Hz}, t_0)$ and the similar shapes of the curves for different $T_{\text{stop}}$ and $t_{\text{stop}}$ in Fig. 4(a), we find that the aging curves at $T < T_{\text{stop}}$ can be scaled equally well through application of a multiplicative factor as they are through an additive factor.

[21] ANGELANI L., Di LEONARDO R., PARISI G. and RUOCCHO, G. *Phys. Rev. Lett.*, **87** (2001) 055502.

[22] KOB W., SCIORTINO F. and TARTAGLIA P., *Europhys. Lett.*, **49** (2000) 590.

[23] DONATI C., SCIORTINO F. and TARTAGLIA P., *Phys. Rev. Lett.*, **85** (2000) 1464.