Memory in the aging of a polymer glass

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Abstract

Low frequency dielectric measurements on plexiglass (PMMA) show that cooling and heating the sample at constant rate give an hysteretic dependence on temperature of the dielectric constant $\epsilon$. A temporary stop of cooling produces a downward relaxation of $\epsilon$. Two main features are observed i) when cooling is resumed $\epsilon$ goes back to the values obtained without the cooling stop (i.e. the low temperature state is independent of the cooling history) ii) upon reheating $\epsilon$ keeps the memory of the aging history ($\textit{Memory}$). The analogies and differences with similar experiments done in spin glasses are discussed.

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The aging of glassy materials is a widely studied phenomenon \[1,2\], which is characterized by a slow evolution of the system toward equilibrium, after a quench below the glass transition temperature \(T_g\). In other words the properties of glassy materials depend on the time spent at a temperature smaller than \(T_g\). In spite of the interesting experimental \[3,4,5,6\] and theoretical progress \[4,7,8\], done in the last years, the physical mechanisms of aging are not yet fully understood. In fact on the basis of available experimental data it is very difficult to distinguish which is the most suitable theoretical approach for describing the aging processes of different materials. In order to give more insight into this problem several experimental procedures have been proposed and applied to the study of the aging of various materials, such as spin-glasses (SG)\[3,6,9\], orientational glasses (OG)\[4,10\], polymers \[1,11\] and supercooled liquids (SL)\[5\]. Among these procedures we may recall the applications of small temperature cycles to a sample during the aging time\[3,4,5,11\]. These experiments have shown three main results in different materials: i) there is an important difference between positive and negative cycles and the details of the response to these perturbations are material dependent \[3,4,11\]; ii) for SG \[3\] the time spent at the higher temperature does not contribute to the aging at a lower temperature whereas for plexiglass (PMMA) \[11\] and OG \[4\] it slightly modifies the long time behavior; iii) A memory effect has been observed for negative cycles. Specifically when temperature goes back to the high temperature the system recovers its state before perturbation. In other words the time spent at low temperature does not contribute to the aging behavior at the higher temperature.

These results clearly exclude models based on the activation processes over temperature independent barriers, where the time spent at high temperature would help to find easily the equilibrium state. At the same time it is difficult to decide which is the most appropriate theoretical approach to describe the response to these temperature cycles \[3\]. For example a recent model explains the results in SG but not in OG and in PMMA \[12\]. In order to have a better understanding of the free energy landscape of SG and OG, a new cooling protocol has been proposed \[6\] and used in several experiments \[3,6,10\]. This protocol, which is characterized by a temporary cooling stop, has revealed that in SG and in OG the low temperature state is independent of the cooling history \[1\] and that these materials keep the memory of the

\[1\] This effect was named \textit{Chaos} in ref.\[3\] but in a more recent paper \[13\] the relevance of chaos for aging has been disputed. The idea of chaos in this context might be inappropriate
aging history (Memory effect)\cite{3}.

The purpose of this letter is to describe an experiment where we use the cooling protocol, proposed in ref.\cite{6}, to show that a memory effect is present during the aging of the dielectric constant of plexiglass (PMMA), which is a polymer glass with $T_g = 388K$ \cite{14,15}. We also compare the behavior of PMMA to that of SG and OG, submitted to the same cooling protocol.

To determine the dielectric constant, we measure the complex impedance of a capacitor whose dielectric is the PMMA sample. In our experiment a disk of PMMA of diameter 10cm and thickness 0.3mm is inserted between the plates of a capacitor whose vacuum capacitance is $C_o = 230pF$. The capacitor temperature is stable within 0.1K and it may be changed from 300K to 500K.

The capacitor is a component of the feedback loop of a precision voltage amplifier whose input is connected to a signal generator. We obtain the real and imaginary part of the capacitor impedance by measuring the response of the amplifier to a sinusoidal input signal. This apparatus allows us to measure the real and imaginary part of the dielectric constant $\epsilon = \epsilon_1 + i \epsilon_2$ as a function of temperature $T$, frequency $\nu$ and time $t$. Relative variations of $\epsilon$ smaller than $10^{-3}$ can be measured in all the frequency range used in this experiment, i.e. $0.1Hz < \nu < 100Hz$. The following discussion will focus only on $\epsilon_1$, because the behavior of $\epsilon_2$ leads to the same conclusions.

The measurement is performed in the following way. We first reinitialize the PMMA history by heating the sample at a temperature $T_{\text{max}} > T_g$. The sample is left at $T_{\text{max}} = 415K$ for a few hours. Then it is slowly cooled from $T_{\text{max}}$ to a temperature $T_{\text{min}} = 313K$ at the constant rate $|R| = |\partial T / \partial t|$ and heated back to $T_{\text{max}}$ at the same $|R|$. The dependence of $\epsilon_1$ on $T$ obtained by cooling and heating the sample at a constant $|R|$, is called the reference curve $\epsilon_r$.

As an example of reference curve we plot in fig.1(a) $\epsilon_r$, measured at 0.1Hz and at $|R| = 20K/h$. We see that $\epsilon_r$ presents a hysteresis between the cooling and the heating in the interval $350K < T < 405K$. This hysteresis depends on the cooling and heating rates. Indeed, in fig.1(b), the difference between the heating curve ($\epsilon_{rh}$) and the cooling curve ($\epsilon_{rc}$) is plotted as a function of $T$ for different $|R|$. The faster we change temperature, the bigger hysteresis we get. Furthermore the temperature of the hysteresis maximum is a few degrees above $T_g$, specifically at $T \approx 392K$. The temperature of this maximum gets closer to $T_g$ when the rate is decreased.

We neglect for the moment the rate dependence of the hysteresis and
we consider as reference curve the one, plotted in fig.1(a), which has been obtained at $\nu = 0.1\,\text{Hz}$ and at $|R| = 20\,\text{K/h}$. The evolution of $\epsilon_1$ can be quite different from $\epsilon_r$ if we use the temperature cycle proposed in ref.[6]. After a cooling at $R = -20\,\text{K/h}$ from $T_{\text{max}}$ to $T_{\text{stop}} = 374\,\text{K}$ the sample is maintained at $T_{\text{stop}}$ for 10h. After this time interval the sample is cooled again, at the same $R$, down to $T_{\text{min}}$. Once the sample temperature reaches $T_{\text{min}}$ the sample is heated again at $R = 20\,\text{K/h}$ up to $T_{\text{max}}$. The dependence of $\epsilon_1$ as a function of $T$, obtained when the sample is submitted to this temperature cycle with the cooling stop at $T_{\text{stop}}$, is called the memory curve $\epsilon_m$. In fig.2(a), $\epsilon_m$ (solid line), measured at $\nu = 0.1\,\text{Hz}$, is plotted as a function of $T$. The dashed line corresponds to the reference curve of fig.1(a). We notice that $\epsilon_m$ relaxes downwards when cooling is stopped at $T_{\text{stop}}$: this corresponds to the vertical line in fig.2(a) where $\epsilon_m$ departs from $\epsilon_r$. When cooling is resumed $\epsilon_1$ merges into $\epsilon_r$ for $T < 340\,\text{K}$. The aging at $T_{\text{stop}}$ has not influenced the result at low temperature.

During the heating period the system keeps the memory of the aging at $T_{\text{stop}}$ (cooling stop) and for $340\,\text{K} < T < 395\,\text{K}$ the evolution of $\epsilon_m$ is quite different from $\epsilon_r$. In order to clearly see this effect we divide $\epsilon_m$ in the cooling part $\epsilon_{mc}$ and the heating part $\epsilon_{mh}$. In fig.2(b) we plot the difference between $\epsilon_m$ and $\epsilon_r$. Filled downwards arrows corresponds to cooling ($\epsilon_{mc} - \epsilon_{rc}$) and empty upward arrows to heating ($\epsilon_{mh} - \epsilon_{rh}$). The difference between the evolutions corresponding to different cooling procedures is now quite clear. The system keeps the memory of its previous aging history when it is reheated from $T_{\text{min}}$. The amplitude of the memory corresponds well to the amplitude of the aging at $T_{\text{stop}}$, but the temperature $T_m$ of the maximum is shifted a few degrees above $T_{\text{stop}}$. We checked that this temperature shift is independent of $T_{\text{stop}}$ for temperatures where aging can be measured in a reasonable time (from $340\,\text{K}$ to $T_g$). This effect can be seen in fig.3 where the difference between $\epsilon_m$ and $\epsilon_r$ measured for three different $T_{\text{stop}}$, is plotted as a function of $T$. We clearly see that $T_m - T_{\text{stop}}$ is independent on $T_{\text{stop}}$. Furthermore the amplitude of the downward relaxation at $T_{\text{stop}}$ is a decreasing function of $T_{\text{stop}}$. It almost disappears for $T_{\text{stop}} < 340\,\text{K}$. For this reason double memory experiments are more difficult in PMMA than in SG. However it has to be pointed out that if two cooling stops are done the system keeps memory of both of them [16].

The memory effect seems to be permanent because it does not depend on the waiting time at $T_{\text{min}}$. Indeed we performed several experiments in which we waited till 24h at $T_{\text{min}}$, before restarting heating, without noticing
any change in the heating cycle. In contrast the amplitude and the position of the memory effect depend on $R$ and on the measuring frequency. As an example of rate dependence, at $\nu = 0.1Hz$ and waiting time at $T_{stop}$ of 10h, we plot in fig.4 the difference $\epsilon_m - \epsilon_r$ as a function of $T$ for three different rates. The faster is the rate the larger is the memory effect and the farther the temperature of its maximum is shifted above the aging temperature $T_{stop}$. Finally we checked the dependence of the memory effect on the measuring frequency. We find that the memory effect becomes larger at the lowest frequency and the positions of the maxima are at the same temperature.

We can summarize the main results of the low frequency dielectric measurements on PMMA: (a) The reference curve, obtained at constant cooling and heating rate is hysteretic. This hysteresis is maximum a few degrees above $T_g$. (b) The hysteresis of $\epsilon_r$ increases with $|R|$. (c) Writing memory: a cooling stop produces a downward relaxation of $\epsilon_1$. The amplitude of this downward relaxation depends on $T_{stop}$ and it decreases for decreasing $T_{stop}$. It almost disappears for $T_{stop} < 330K$. (d) When cooling is resumed $\epsilon_1$ goes back to the cooling branch of the reference curve. This suggests that the low temperature state is independent on the cooling history. (e) Reading memory: upon reheating $\epsilon_1$ keeps the memory of the aging history and the cooling stop (Memory). The maximum of the memory effect is obtained a few degrees above $T_{stop}$. (f) The memory effect does not depend on the waiting time at low temperature but it depends both on the cooling and heating rates $[16]$. The memory effect increases with $|R|$.

These results can be explained by a hierarchical free energy landscape, whose barriers growth when temperature is lowered $[3, 4]$. However the dependence of the memory effect and the hysteresis on $|R|$ and the independence on the waiting time at $T_{min}$ means that, at least for PMMA, the free energy landscape has to depend not only on temperature but also on $|R|$. The existence of the hysteresis and temperature shift of the memory effect could also be explained by a dependence of the landscape on the sign of the rate (and not only on its magnitude). Many models $[3, 8, 17, 18]$ and numerical simulations $[19, 20]$ do not take into account this dependence because they consider just a static temperature after a quench. In contrast points a),b),e) and f) indicate that whole temperature history is relevant too. Other models based on the idea of domains growth explain the rate dependence but not the memory effect $[13, 21]$. Analogies between point a-b) for the hysteresis and point e-f) for the rate dependence of the memory effect leads to a new interpretation of hysteresis,
which can be seen as the memory of aging at a temperature $T_{\text{stop}} \approx T_g$. Indeed, in a free energy landscape model, when cooling the sample just above $T_g$ the system is in its equilibrium phase, that is in a favorable configuration at this temperature. If this configuration is not strongly modified by aging at lower temperatures then, when heating back to $T_g$, the system keeps the memory of this favorable state, just as it does in the memory effect.

It is interesting to discuss the analogies and the differences between this experiment and similar ones performed on SG [6, 9] and on OG [10]. It turns out that, neglecting the hysteresis of the reference curve of PMMA and of OG, the behavior of these materials is quite similar to that of SG. During the heating period PMMA, SG and OG keep the memory of their aging history, although the precise way, in which history is remembered, is material dependent. Furthermore, in these materials the low temperature state is independent on the cooling history (same response, same aging properties [11]). One can estimate the temperature range $\delta T$ where the material response is different from that of the reference curve because of the cooling stop. It turns out that the ratio $\delta T/T_G$ is roughly the same in PMMA, in SG and in OG, specifically $\delta T/T_G \approx 0.2$. The important difference between SG and PMMA is that the amplitude of the downward relaxation is a function of $T_{\text{stop}}$ in PMMA and it is not in SG.

As a conclusion the "memory" effect seems to be an universal feature of aging whereas the hysteresis is present in PMMA and in OG but not in all kinds of spin glasses. It would be interesting to know if these effects are observed in other polymers and in supercooled liquids, and if the hysteresis interpretation in terms of a memory effects hold for other materials. As far as we know no other results are available at the moment.

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References

[1] L.C. Struik, Physical aging in amorphous polymers and other materials (Elsevier, Amsterdam, 1978).

[2] Spin Glasses and Random Fields, edit by A. P. Young, Series on Directions in Condensed Matter Physics Vol.12 ( World Scientific, Singapore 1998).

[3] M. Lederman, R. Orbach, J.M. Hammann, M. Ocio, E. Vincent, Phys. Rev. B, 44, 7403 (1991); E. Vincent, J. P. Bouchaud, J. Hammann, F. Lefloch, Phil. Mag. B, 71, 489 (1995); C. Djuberg, K. Jonason, P. Nordblad, Eur. Phys. J. B 10, 15 (1999).

[4] F. Alberici, P. Doussineau, A. Levelut Europhysics Lett. 39, 329 (1997).

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

[6] K.Jonason, E. Vincent, J. Hamman, J. P. Bouchaud, P. Nordblad, Phys. Rev. Lett. 81, 3243 (1998).

[7] J. P. Bouchaud, L.F. Cugliandolo, J. Kurchan, M. Mézard, in Spin Glasses and Random Fields, [2], and references therein.

[8] M.Mézard, G. Parisi, M. A. Virasoro, in Spin Glasses Theory and Beyond, World Scientific Lecture Notes in Physics Vol.9 ( World Scientific, Singapore 1987).

[9] T. Jonsson, K. Jonason, P. Nordblad, Phys. Rev. B 59, 9402 (1999); T. Jonsson, K. Jonason, P. Jonsson, P. Nordblad, Phys Rev. B 59, 8770 (1999).

[10] P. Doussineau, T. Lacerda-Aroso, A. Levelut, Europhys. Lett., 46, 401 (1999).

[11] L. Bellon, S. Ciliberto, C. Laroche, cond-mat/9905160.

[12] L. F. Cugliandolo, J. Kurchan, Phys. Rev. B 60, 922 (1999).

[13] E. Vincent, V. Dupuis, M. Alba, J. Hamman, J. P. Bouchaud, to be published in Europhysics Letters (cond-mat/9908030).
In a temperature interval of a few degrees around $T_g$ the PMMA Young modulus changes of several orders of magnitude \[14\]. This $T_g$ is consistent with the experimental evidence \[11\] that for $T < T_g$ PMMA presents aging whereas for $T > T_g$ PMMA relaxes to its equilibrium in less than 5h.

More details will be given elsewhere.

D. S. Fisher, D. A. Huse, Phys. Rev. Lett. 56, 1601, (1987).

A. J. Bray, M. A. Moore, Phys. Rev. Lett. 58, 57 (1987).

E. Marinari, G. Parisi, J.J. Ruiz-Lorenzo, F. Ritort Phys. Rev. Lett. 76, 843 (1996); E. Marinari, G. Parisi J.J. Ruiz-Lorenzo, in *Spin Glasses and Random Fields* pp.59-98; E. Marinari, G. Parisi, J. J. Ruiz-Lorenzo Phys. Rev. B. 58, 14852 (1998).

W. Kob, J.L. Barrat, Phys. Rev. Lett. 78, 4581 (1997).

J. P. Bouchaud,” Aging in glassy systems: new experiments, simple models and open questions ”, \texttt{cond-mat/9910387}. 

[14] N. G. McCrum, B. E. Read, G. Williams *Anelastic and Dielectric Effects in Polymeric Solids*, (Dover 1991)

[15] D. S. Fisher, D. A. Huse, Phys. Rev. Lett. 56, 1601, (1987).

[18] A. J. Bray, M. A. Moore, Phys. Rev. Lett. 58, 57 (1987).

[19] E. Marinari, G. Parisi, J.J. Ruiz-Lorenzo, F. Ritort Phys. Rev. Lett. 76, 843 (1996); E. Marinari, G. Parisi J.J. Ruiz-Lorenzo, in *Spin Glasses and Random Fields* pp.59-98; E. Marinari, G. Parisi, J. J. Ruiz-Lorenzo Phys. Rev. B. 58, 14852 (1998).

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

[21] J. P. Bouchaud,” Aging in glassy systems: new experiments, simple models and open questions ”, \texttt{cond-mat/9910387}. 

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Figure 1: (a) Evolution of $\varepsilon_r$ at $\nu = 0.1 Hz$ as a function of $T$. Reference curve obtained with $|R| = 20 K/h$. (b) Hysteresis of the reference curve (difference between the heating and cooling curves $\varepsilon_{rh} - \varepsilon_{rc}$) for 3 different $|R|$: $5 K/h (\triangle)$, $10 K/h (\circ)$ and $20 K/h (\triangledown)$. 
Figure 2: (a) Evolution of $\epsilon$ at $\nu = 0.1Hz$ as a function of $T$. The dashed line corresponds to the reference curve ($\epsilon_r$) of Fig. 1(a). The solid bold line corresponds to a different cooling procedure: the sample is cooled, at $R = -20K/h$, from $T_{max} = 374K$, where cooling is stopped for 10h. Afterwards the sample is cooled at the same $R$ till $T_{min}$ and then heated again at $R = 20K/h$ till $T_{max}$. (b) Difference between the evolution of $\epsilon_r$ and $\epsilon_m$. Downward filled arrows correspond to cooling ($\epsilon_{mc} - \epsilon_{rc}$) and upward empty arrows to heating ($\epsilon_{mh} - \epsilon_{rh}$).
Figure 3: Dependence on $T_{\text{stop}}$. Difference between $\epsilon_r$ and $\epsilon_m$ for three different cooling stops at $\nu = 0.1Hz$, $|R| = 10K/h$ and $t_{\text{stop}} = 10h$. (a) Writing memory (cooling) : $\epsilon_{mc} - \epsilon_{rc}$ with $T_{\text{stop}} = 344K$ (▲), $T_{\text{stop}} = 364K$ (●) and $T_{\text{stop}} = 374K$ (▼). (b) Reading memory (heating) : $\epsilon_{mh} - \epsilon_{rh}$ of $T_{\text{stop}} = 344K$ (△), $T_{\text{stop}} = 364K$ (○) and $T_{\text{stop}} = 374K$ (▽).
Figure 4: Dependence on the cooling and heating rate. Difference between \( \epsilon_r \) and \( \epsilon_m \) (aging at \( T_{\text{stop}} = 374K \) for 10h) measured at \( \nu = 0.1Hz \) for 3 \( |R| \).

(a) Writing memory (cooling) : \( \epsilon_{mc} - \epsilon_{rc} \) at 5K/h (▲), 10K/h (●) and 20K/h (▼).

(b) Reading memory (heating) : \( \epsilon_{mh} - \epsilon_{rh} \) at 5K/h (△), 10K/h (○) and 20K/h (▽).