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Aging and memory effects in a clathrate

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Abstract. The out-of-equilibrium low-frequency complex susceptibility of the orientational glass methanol(73%)-β-hydroquinone-clathrate is studied using temperature-stop protocols in aging experiments. Although the material does not have a sharp glass transition aging effects including rejuvenation and memory similar to the effects in spin glasses are found at low temperatures.

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1 Introduction

Physical aging has attracted a lot of attention and gave and gives rise to many discussions. The basic observation is that the behavior of the physical response functions like magnetization, polarization or the corresponding susceptibilities is time and waiting time dependent. It depends on a waiting time t_ω spent before a perturbation (a magnetic or electric field) has been applied or after it has been switched off. A spin glass can even memorize some of the features of the way the system had been prepared. A lot of effort has been made to carry out and understand aging experiments in spin glasses [1,2,3]. The present study deals with aging, rejuvenation and memory effects in a dipolar glass, namely methanol($x = 0.73$)-β-hydroquinone-clathrate.

In the β-hydroquinone-clathrates, C- and O-rings enclose an almost spherical cavity of about 4 Å diameter [4]. A large variety of guest molecules can reside in the cages, ranging from H_2, O_2 and noble gas atoms to large molecules as CH_3CN [5] and CH_3Br and even C_{60} [6]. For the present study we enclosed methanol as a guest molecule. Figure 1 shows schematically the methanol molecule in its hydroquinone cage. The methanol molecule has a dipole moment of $d = 1.7$ D. Due to a C_{3i} site symmetry in the cage center, the methanol and with it its dipole moment has six orientations in the cage. The methanol molecule performs head-tail flips and in addition a threefold rotation about the cage center. The behavior of the methanol-clathrate is determined

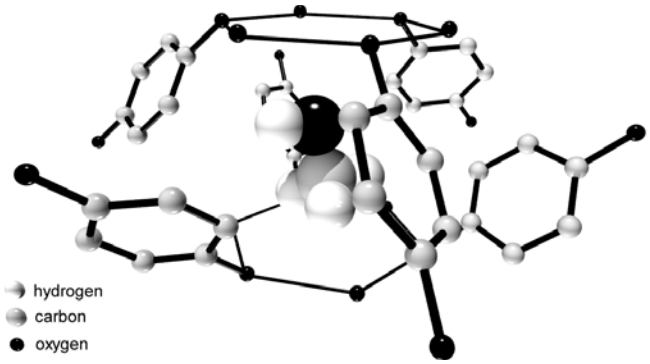

Fig. 1. The methanol molecule (CH_3OH) in the quinone cagework. For the atoms of the methanol molecule, the Van-der-Waals radius is plotted, the C- and O-atoms of the cagework are plotted as a stick and ball model, H-atoms are omitted.

and can be understood considering the electric dipole-dipole interaction (EDD) between the methanol-dipoles, only [7,8]. The methanol molecule can reorient relatively freely and the interaction with the surrounding host lattice can be neglected. In that sense the methanol-β-hydroquinone-clathrate represents a dielectric model system: you deal with well defined dipoles on the sites of a regular lattice and a well defined interaction between them (EDD). The methanol-clathrate condensates in a rhombohedral $R\bar{3}$ structure. At $T = 65$ K the dipole system orders *via* a first order phase transition in an antiferroelectrically ordered structure. It basically consists of ferroelectrically ordered dipole chains running along the hexagonal c-axis [7,8]. In the basal plane the chains

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are arranged in a triangular pattern. The antiferroelectric interaction between the chains can not be satisfied on a triangular lattice and yields to strong frustration.

Clathrates with occupation less than about 97% can be grown. The empty β-hydroquinone-clathrate is not stable, the cages collapse. The methanol-clathrate tolerates occupations down to about 35% before collapsing. Whereas the higher concentrated samples down to about 76% show a first order phase transition into an antiferroelectrically ordered phase, the lower concentrated samples freeze into dipolar glasses. In the 40% sample, the molecules simply freeze into single particle potentials without any interaction between the dipoles and it is of the random field type. In the 73% sample, the interactions between the dipoles still play a role (within experimental time scales) and it is of the random bond type. With it, the methanol-($x = 0.73$)-β-hydroquinone-clathrate is conceptually close to its magnetic pendants, the spin glasses. Motivated by aging experiments in spin glasses we performed aging and memory experiments in the diluted methanol-clathrate. The paper is organized as follows: Section 2 describes the experimental set-up. In Section 3 we present our aging and memory experiments in the diluted methanol-clathrate. In the discussion in Section 4 we introduce a domain model to explain aging effects in dipolar glasses and compare the effects with aging in spin glasses. Section 5 gives a short summary.

2 Experimental

Single crystals of methanol($x = 0.73$)-β-hydroquinone-clathrate have been grown from a saturated solution of quinol, methanol and n-propanol at 313 K. The propanol molecules are not incorporated into the lattice but merely control the percentage of void cavities. The samples were prepared in the form of thin parallel plates ($d \sim 0.5$ mm) with faces perpendicular to the hexagonal c-axis. With gold electrodes deposited on these faces they formed capacitors with a capacitance of about 0.4 pF. For the measurement of the frequency-dependent permittivity, a Solartron impedance analyzer FRA 1260 in combination with an interface (Chelsea) has been employed. The samples were placed into a closed-cycle refrigerator with a temperature stability of some mK.

We measured real and imaginary part of the dielectric constant, $\varepsilon_c'(\nu)$ and $\varepsilon_c''(\nu)$, along the hexagonal c-axis for frequencies from $\nu = 0.2$ Hz up to $\nu = 200$ Hz. Figure 2 shows the temperature dependence of the imaginary part, $\varepsilon_c''(\nu)$. The relaxation processes are characterized by a rather broad distribution of relaxation times τ and obey an Arrhenius law (with the "pseudospin" flip-rate $\tau_0^{-1} = 9 \times 10^{10}$ s^{-1} and an energy barrier $E_A = 828$ K) rather than a Vogel-Fulcher-behavior (see also [9]) that you would expect in a dipolar glass with a clear transition temperature T_g [10]. The distribution of relaxation times broadens with temperature as the area under the loss peaks decreases with lowering temperature. Although there is no clear transition into a dipolar glass state we find glassy dynamics at low temperatures. The effective energy barrier E_A decomposes into a contribution of the crystal field (E_{loc}) and a contribution of the interaction between the dipoles, $E_A \approx E_{loc} + 4J_c$, J_c being a coupling parameter [7]. In our sample, the freezing is dominated by random interactions ($E_{loc} \approx 210$ K, $4J_c \approx 620$ K) and should be close to spin-glass-like.

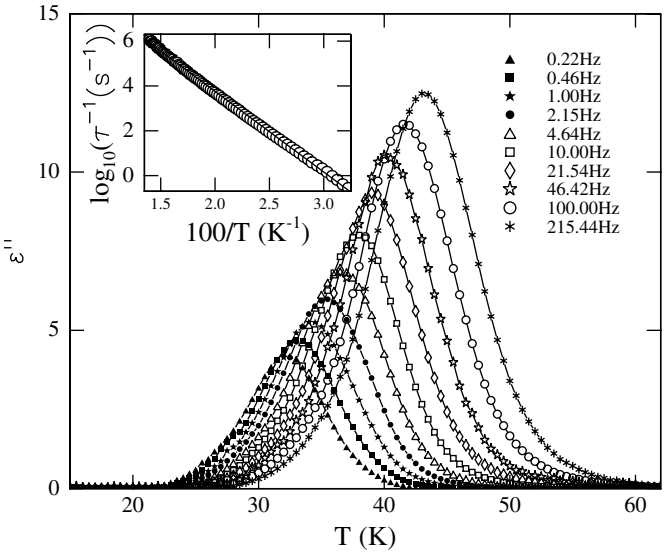

Fig. 2. Temperature dependence of the imaginary part of the dielectric constant, ε_c''. The insert shows the inverse average relaxation time τ^{-1} as a function of $1/T$ (determined from the temperature of maximum ε_c'' for frequencies ranging from 0.1 Hz-1 MHz). (From [9]).

3 Aging and memory experiments

To study aging effects like memory and rejuvenation, the following temperature-time-protocol was applied: we chose $\nu = 2$ Hz as measurement frequency. From $T = 40$ K, well above the maximum of $\varepsilon''(2$ Hz) in Figure 2, we slowly cooled down. While cooling we continuously measured the dielectric susceptibility $\varepsilon''(\nu)$. Figure 3 shows the corresponding measurement, ε'' is normalized to an uninterrupted reference curve to make the small effect of just 1–2% clearly visible. There is basically no difference between aging in the real and imaginary of the susceptibility. Aging is normally a bit more pronounced in the out-of-phase component and we will in the following concentrate on this. At $T_a = 31.5$ K, below the relaxation maximum, we stopped and aged the system for the time $t_\omega = 50\,000$ s. As the system with time can find lower energy valleys and comes closer to equilibrium the dielectric response decays. The insert in Figure 3 shows the decay of $\varepsilon''(\nu)$ with time. When we resumed cooling after a few Kelvin the system found back to the uninterrupted reference curve, it showed rejuvenation. Aging at T_a obviously had no effect on the age at other temperatures. In spin glasses this is called chaos. We then cooled down to the base temperature of the cryostat ($T = 5$ K). At the

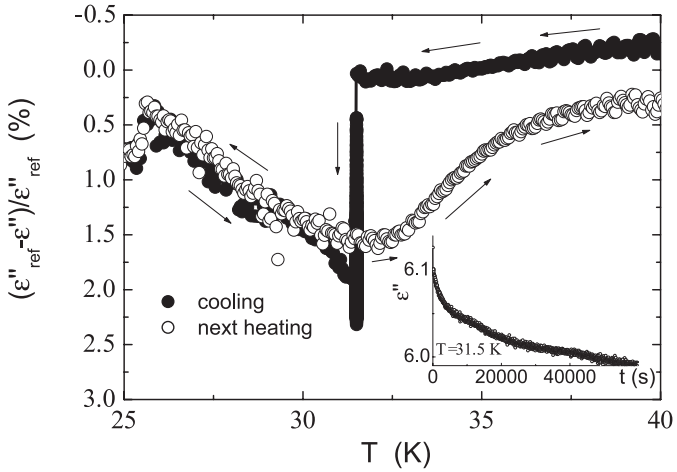

Fig. 3. Difference $(\varepsilon''_{ref}(T) - \varepsilon''(T))/\varepsilon''_{ref}(T)$. The insert shows the time evolution of ε'' at $T_a = 31.5$ K. (From [9]).

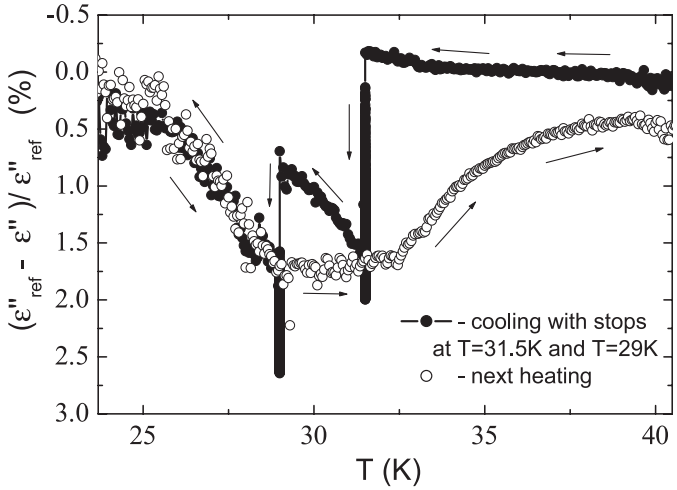

Fig. 4. Double aging/memory experiment in methanol(73%)-clathrate. The dependence $(\varepsilon''_{ref}(T) - \varepsilon''(T))/\varepsilon''_{ref}(T)$ vs. the temperature is shown for cooling and heating runs. The cooling run was twice interrupted at the temperatures $T_{a1} = 31.5$ K and $T_{a2} = 29$ K for the waiting time of $t_\omega = 50000$ s, respectively (From [9]).

immediately following re-heating, we find a broad dip in the dielectric loss centered at the aging temperature T_a. The system remembers that it has been aged here before and already came closer to equilibrium at T_a. This is called memory. We also performed double step aging and memory experiments (see Fig. 4). After aging at a temperature T_{a1} we resumed cooling and aged at a second lower temperature T_{a2}. When halting at T_{a2} there again is a time evolution of ε'' and the system rejuvenated when we resumed cooling after $t_\omega = 50000$ s. The memory dip when re-heating is even broader than before. The distance of the two temperatures T_{a1} and T_{a2} is not large enough to separate the two memory dips well. These effects would be trivial if there was no time evolution of ε'' at the second aging temperature T_{a2}. Then the system was completely frozen and all quantities should indeed take their previous values when the system is heated back. The combination of aging, rejuvenation and further time evolution at the second temperature and memory is puzzling.

4 Discussion

We find aging, rejuvenation and memory in methanol-($x = 0.73$)-β-hydroquinone-clathrate similar to the effects in spin glasses even there is no clear evidence that we are in a dipolar glass state. Nevertheless the dilution in combination with the long ranged antiferroelectric interactions leads to a large number of metastable states and strong frustration and we expect glassy dynamics at low temperatures.

In spin glasses in a real space picture aging, rejuvenation and memory can be understood by inhomogeneous and frustrated interactions [11]. Because of several exchange paths with different strength and signs, the interaction between two spins becomes strongly temperature dependent and can even change sign. When changing the temperature the complex pattern of interactions typical for a spin glass changes drastically. Two patterns at two different temperatures are completely uncorrelated and there is rejuvenation or chaos. The inhomogeneous distribution of interactions leads to the appearance of so-called memory spots. Within the framework of interactions two strongly bound spins will have an extremely large relaxation time $\tau_{mem} = \tau_0 \exp(\Delta E/T)$ (τ_0 is a microscopic time scale) corresponding to the high energy barrier ΔE over which they have to relax. When returning to the aging temperature these nucleation spots serve to re-establish the already aged interaction pattern and there is memory. For aging in dipolar glasses a domain model has been proposed [12,13]. The basic idea is the existence of polarization domains, *i.e.* areas of strongly coupled dipoles (even though the interaction is random and the domains will not be comparable to ordered domains as *e.g.* in a ferromagnet). The domain wall movement is strongly impeded by static random fields. In our case the random fields arise from the partial occupation. The neighborhood of statistically empty and filled cavities leads to a random distortion of the crystal field in the cages. The growth of domains over energy barriers is a thermally activated process. Only molecules in the domain walls contribute to the dielectric response, molecules from inside the domains are already frozen. The dielectric response ε'' is inversely proportional to the domain size R, $\varepsilon'' \propto 1/R(t)$, as the volume fraction of wall molecules reduces when domains grow. At each temperature T there is an equilibrium domain size $\xi(T)$. ξ is the larger the lower the temperature, $\xi(T) \propto 1/\sqrt{T}$. All domains grow towards their equilibrium size. Their evolution stops when they have reached $\xi(T)$. In a very simplified picture there are fast growing, slow growing and frozen domains as prototypes for the different energy barriers. In a more realistic model, a distribution of energy barriers, a distribution of domain sizes and a size dependent growth rate have to be taken into account. But even this very simple picture can qualitatively explain

the observations in methanol($x = 0.73$)-β-hydroquinone-clathrate. When aging at $T_a = 31.5$ K in Figure 3, the fast and the slow domains grow towards their equilibrium size $\xi(31.5\ \mathrm{K})$ and the dielectric response decays. At the end of the aging period the fast domains will almost have reached $\xi(31.5\ \mathrm{K})$. When cooling is resumed the equilibrium size enlarges and the domains will fall out of equilibrium again. As the system is cooled and domain growth is a thermally activated process fast domains will become slow and slow domains will freeze. The pattern of "active" domains changes and the system rejuvenates. The domain pattern that has grown during t_ω at T_a will freeze and is imprinted in the system. When re-heating, at or close to T_a the domains will become mobile again. Domains will just continue growing where aging has been interrupted at the end of t_ω and produce memory. One remarkable difference between the aging features in dipolar glasses and spin glasses is that in dipolar glasses memory is not erased when the temperature is raised moderately. This is in strong contradiction to aging in spin glasses where a positive temperature step erases memory and an indication for different underlying mechanism.

5 Conclusion

In methanol($x = 0.73$)-β-hydroquinone-clathrate we find aging, rejuvenation and memory effects similar to the effects found in spin glasses. Even if the observations are similar the basic mechanism of aging in dipolar glasses and spin glasses is different. In spin glasses for instance you deal with a pure random bond system where the complex patterns of interactions at different temperatures are completely uncorrelated in contrast to the domains in dipolar glasses or random ferromagnets. Even in methanol-($x = 0.73$)-β-hydroquinone-clathrate where the behavior is dominated by the dipole-dipole interaction the coupling of the pseudospins to the random fields is not negligible. That leads to differences in the observations and possible explanations and models. Because of the model character of the methanol-clathrate it is certainly worth to scrutinize closely the details of the microscopic mechanism underlying these aging effects. Nevertheless additional experiments are needed to complete our understanding of aging in the diluted methanol-clathrate.

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