Density wave system: slush or real glass

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Abstract. - We show that the relaxational dynamics as exhibited in the enthalpy relaxation of the density wave compounds at very low temperatures ($T < 1\text{K}$) is very similar to that one occurring in disordered systems such as glassy polymers or spin glasses. We discuss these similarities, as well as some peculiarities, in the frame of secondary relaxational processes as genuine features of glass formers below their glass transition temperature. This approach is strongly supported by recent direct evidence for the existing glass transition brought about by means of calorimetric and dielectric measurements.

1. Introduction

In the last decade it became quite customary to talk on "glassy behaviour" of charge-density-waves (CDWs). Recently the same behaviour has been also attributed to spin-density-waves (SDWs). A characteristic feature of a DW (both CDW and SDW) is the very wide time range for relaxation processes. In glasses, relaxation occurs continuously from atomic time scales to a characteristic time, which in the vicinity of freezing temperature T_g goes beyond laboratory time scales. DW systems show anomalously slow relaxations in very different energy-time windows. But, a system for which long time relaxations are involved is not necessarily a glass; it may just have a glass-like behaviour (as a slush). Then it remains the central question ; Is there a transition from a "slush" to a real glass?

In this communication we show that the properties of DW ground state are drastically changed at very low temperatures and that at least in organic SDW compound $(\text{TMTSF})_2\text{PF}_6$ (in short PF_6) the reason is the occurrence of a real glass transition. We reconcile two relaxational processes observed at low temperatures into the consistent picture of the experimental glass transition. The low frequency dielectric relaxation shows a characteristic freezing out identified as the primary processes in glasses. In the same temperature range the secondary slow enthalpy relaxation appears as an universal property of the glassy state. Typical aging features will be discussed in comparison to other glassy formers as polymers (PG), ionic glasses (IG) and spin glasses (SG). These effects originate from the DW low energy excitations (LEE) which contribute to the specific heat and make it strongly time dependent. For this reason in the following we prefer to use a more appropriate term - enthalpy susceptibility - instead of specific heat. Finally, we hold out a simplified scenario for the DW glass transition.

2. Low temperature thermodynamic properties

There are many different experimental evidences (as well as theoretical presumptions) of the existence of metastable states in DWs in the whole temperature range between their phase transition down to the lowest temperatures. The number of metastable states corresponds to the number of relative minima of the free energy. The complexity of the free-energy landscape in configuration space increases as T is lowered. Indeed very rich spectra of the effects revealing the glassy nature of the DW ground state have been found in low temperature ($T < 10\text{K}$) specific heat experiments [1].

LEE play the dominant role in the enthalpy susceptibility and the enthalpy relaxation at $T < 1$ K. Here we specify the mean features:

- (i) an extra-contribution to phonon specific heat which strongly depends on the duration of the heat perturbation (heat pulses used for the measurement);
- (ii) a non-exponential decay after the perturbation has been switched off;
- (iii) a dependence on the time during which the thermal perturbation has been applied;
- (iv) the evolution of the relaxation indicates a crossover between a non-equilibrium state and the thermodynamical equilibrium state when the system has been allowed to "age";
- (v) the relaxation is thermally activated with an activation energy of ~ 1 K (depending on the duration of the perturbation).

In next two paragraphs we are going to describe in more detail the effect of aging on the enthalpy relaxation and the enthalpy susceptibility. In comparison with other glasses these properties well represent a real "DW glass".

2. 1. Aging

The phenomenon of aging known to occur in PG has been also discovered 10 years ago in SG by Lungren et al [2] and more recently in CDW [3] and in high critical temperature superconductors [4]. After the perturbation (mechanical strain, magnetic field or heat pulse) has been switched off, one finds that the system relaxes extremely slowly and nonexponentially. In addition, these relaxation curves are not uniquely determined : they turn out to depend on the waiting time t_w . Depending on the type of experiment t_w has been defined in various ways:

- (1) the time that has elapsed between the switch on and switch off of the perturbation
- (2) the time during which the system has evolved at fixed T before being probed by a small perturbation.

For the second case, the same definition of t_w holds for two types of experiment: for the dynamics of the relaxation function (decay after switch off of the perturbation) or for the frequency-dependent response as ac susceptibility or noise measured at constant frequency ν , i.e. at a constant observation time of order $t \sim \nu^{-1} \ll t_w$.

Fig.1.- a) Normalized enthalpy relaxation as a function of the duration of the heat flow in $(\text{TaSe}_4)_2\text{I}$ at $T=0.15\text{K}$ shows a typical aging effect ; b) Decay of stress generated by instantaneous application of strain after different waiting times at the same temperature ($T < T_g$) for ionic glass $40\text{AgI}.60\text{AgPO}_3$ (taken from ref. 5)

Figure 1a shows the normalised relaxation of the enthalpy of $(\text{TaSe}_4)_2\text{I}$ at $T = 0.15$ K chosen here to represent similar effects (slightly different only in their intensities) observed in TaS_3 , NbSe_3 and finally in PF_6 [1,3,12]. ΔT_0 is the small increase of temperature ($\Delta T_0/T_0 \lesssim 5\%$) induced by a constant heat flow through the sample at $T = T_0$ during the time t_w defined above as for the case (1). When switched off the relaxation $\Delta T/\Delta T_0$ shows a strong dependence on t_w . For comparison we show on figure 1b a waiting time dependent behaviour for one IG system. There is an evident similarity of the relaxational processes in both systems regardless of different mean relaxation times and quite different measured properties. For IG compound aging has been performed [5] as defined for the case (2): the sample ages at some temperature

$T < T_g$ for different t_w prior to instantaneous application of a strain. The stress decay is slower for the longer aging. The aging effects are primarily due to the fact that the system has not reached its equilibrium state at time of the measurement. After sufficient time, the sample reaches thermodynamic equilibrium (TDE), i. e. ergodicity is restored, and the decay function becomes constant and reproducible. Certainly, aging process disappears when the total aging time is of the order of the largest relaxation time of the system as shown further in figure 2.

Here, we should say few words more on the definition of aging and the problem of non-linearity in order to avoid some misleadings. The characteristic feature of the relaxation in SGs is a maximum of the relaxation rate at an observation time almost equal to the wait time [2]. Aging is a way of "scanning" the phase space structure of a complex system. In the conditions of "true" aging the phase space is effectively infinite and the inflection point in the relaxation should occur exactly at t_w . This happens only in an ideal case. SGs are known as non-stationary and non-ergodic systems but still they obey quite well the linear-response [6]. However, the non-linear character is accounted for by allowing the relaxation times to depend both on T and on t_w or the average structural state of the system (what will be again discussed in the next paragraph for the effect of isothermal annealing). The large width of the distribution of relaxation times is at the origin of the non-exponential character of the relaxation in complex systems. The width is also inversely proportional to the stretched exponent β . The distribution can be calculated from the logarithmic derivative of the relaxation function. We showed that in CDWs the shape and the maximum of the distribution strongly depend on T and t_w [3]. The exceedingly slow dynamics of DW systems implies that most experiments are performed on a system in dynamic non-equilibrium. One should therefore be careful to interpret experimental data as being representative of a DW at TDE. In our experiments we can follow how DW reaches TDE after saturation of aging effect at different temperatures [3].

Fig.2.- a) Dependence of the maximum of the relaxation rate $d(\Delta T/\Delta T_0)/d\log t$ on t_w - the time spent under a small heat perturbation (few mK) at different temperatures for $(\text{TaSe}_4)_2\text{I}$. Inset shows the Arrhenius plot of the equilibrium relaxation times t_e . b) Double logarithmic representation of aging time shift factor a_{te} , versus aging time for an epoxy glass at different temperatures below its glass transition temperature (taken from ref. 7)

In figure 2 we compare similar effects on aging in $(\text{TaSe}_4)_2\text{I}$ and in one PG. The "true" aging regime is spread over longer time as the temperature is decreased before being interrupted when the system reaches TDE. The cross-over from aging to non-aging behaviour also exists and it looks quite abrupt in the minutes time scale for epoxy glasses, as shown on figure 2b. For each $T < T_g$ where the sample has been allowed to age, it is possible to define time t^* , for the glass to reach its "equilibrium" state. In SGs, on approaching T_g the edge of the relaxation rate drastically increases. Below T_g , as the consequence of enormously long relaxation time, relaxation "never" reaches zero and a "true" aging appears. For DWs this evolution is smooth (in seconds time scale), contrary to SGs, as a broader temperature range is accessible in which the experimental time window for aging effects ($1-10^5\text{s}$) is in the range of the relaxation time of the compound. It is of a great importance to get a better understanding of the large variety of experimental aging effects. One of possible directions is in the characterisation of the phase space. The corresponding scales for probing the DW phase space are given by the relaxation times when the system reaches TDE and the aging is interrupted (t_e). The temperature behaviour of this relaxational process (inset in figure 2a)

shows that DW degrees of freedom are still active below 0.5K with an activation energy of ~ 1 K (more details in ref. 1, 3 and 12).

In fact the cross-over from a non-equilibrium to an equilibrium regime in the aging phenomenon observed by us has been designated as "interrupted aging" by Bouchaud in his phenomenological model on weak ergodicity breaking and aging in disordered systems [8]. Quantifying the idea that aging stops when the exploration of the phase space is completed this model allows to estimate the number of metastable states in a complex system and its temperature dependence. The ergodic time t_e corresponds to the time for which all accessible metastable states in the corrugated phase space bottom have been visited and so it is related to the number of available states and it is a measure of the "complexity" of the system. The systematic deviation from a simple t/t_w scaling which would correspond to "real aging" is given through the exponent μ , so that obtained scaling t/t_w^μ can be explained provided one takes into account the finite number of available metastable states, or in other words, that aging is interrupted in a certain fraction of subsystems. On figure 3 we compare the relaxational curves obtained in $(\text{TaSe}_4)_2\text{I}$ and SG system Ag:Mn.

Fig.3.- a) Enthalpy relaxation in $(\text{TaSe}_4)_2\text{I}$ at $T=0.15\text{K}$ can be scaled for $t_w=14\text{h}$ and 32s with $\mu=0.25$.

b) Thermoremanent magnetization relaxation in Ag:Mn 2.6% at 9K, as a function of $\log(t/t_w)$ for different waiting times shows a systematic shift towards faster relaxation as t_w increases (taken from ref.9)

The inversion of the curves for longer and shorter waiting times for Ag:Mn in the simple t/t_w scaling shows that $1 > \mu \approx 0.9$. For DW system this exponent is much smaller and strongly depends on T ($\mu = 0.25$ for $(\text{TaSe}_4)_2\text{I}$ at $T=0.15\text{K}$) so that only at the lowest temperatures (below our range of measurement) one approaches a situation similar to SG. Another quantification is possible through the ergodic time t_e which in PF_6 reaches a value of 10^5s at 0.1K while in SG compounds as Ag:Mn and Cr:In this ergodic time is 10^6s near T_g [9]. We can conclude that the "complexity" of DWs will only reach that one of SGs at very low temperature i. e. below 0.1K . The apparent similarity, together with some particularities, of the very slow relaxation in DW systems and in SG deserves special consideration. Above, we pointed out that all these effects are even more pronounced in PF_6 which is a prototype SDW system. On the one hand it is striking to find the characteristics of SG in a system with long range SDW order and on the other hand to know that an attempt has been made to treat the metallic SG as a short-range "frustrated" SDW [10].

2. 2. Specific heat or enthalpy susceptibility

After the previous paragraph on the enthalpy relaxation, now we are going to consider the enthalpy response function. The first part concerns the estimation of the LEE contribution as some kind of "specific heat spectroscopy" which reflects the aging effects. The second part presents a quite particular property of the short pulse enthalpy susceptibility that we have observed in PF_6 in the region of a calorimetric glass transition [13].

In the temperature range where LEE contribution overcomes the regular phonon contribution to the specific heat, the non-exponential enthalpy decay allows quite arbitrary determination of corresponding C_p . Residual " C_p " measured by the transient heat pulse technique on a time span of $1\text{--}10\text{s}$ which presents only the contribution from the fastest LEE modes is shown to obey a power law T^γ , with exponent $\gamma \leq 1$, and

with an amplitude in the range of glassy materials [1, 11]. However, as it has been said above, there is a large contribution of very slow modes on lowering the temperature. The kinetics and consequently the value of the "heat capacity" which can be calculated from the total heat release is then dependent upon the duration of the thermal perturbation. Analysing the same enthalpy decays as used for the investigation of the aging, we can follow how the heat is poured out into more and more LEE modes. Because of non-equilibrium conditions revealed by aging, it is more appropriate to consider the enthalpy susceptibility. It has been calculated by the integration of total energy release through the heat link, following a thermal perturbation of different durations, from second to several hours. The enthalpy susceptibility increases with the duration of the perturbation reaching a maximum value when aging has been stopped and the system has reached TDE. As shown on figure 4a the difference between the TDE value and that one obtained for the shortest pulses progressively increases with decreasing temperature and in TaS₃ these two values differ by one order of magnitude at 0.1 K [1, 11b]. In PF₆ this effect is even larger (almost two orders of magnitude at 0.1 K).

Fig.4.- a) Total enthalpy susceptibility of o-TaS₃, measured on different time spans. (•) usual transient technique, i. e. response to a heat pulse of duration of 1 s or less. Other symbols (Δ , x, $\square$, $\circ$): " C_p " is calculated by the integration of total energy release through the heat link, following a thermal perturbation of different durations, from 1 seconde to several hours. Maximum values correspond to the thermodynamical equilibrium state reached by the LEE. b) Temperature dependence of total enthalpy susceptibility in the short pulse regime of PF₆ in C/T^3 diagram in the vicinity of the glass transition. Two features are pronounced; the overshoot on reheating accompanied by an isothermal time evolution of " C_p " for different annealing (waiting) times.

We said in the preceeding paragraph that the distribution of relaxation times obtained from relaxation rates in DWs [3,12] at $T < 1$ K seems to change both with T and the duration of pulses turning up the underlying nonlinearities. Another manifestation of the non-linear character of the response we found in PF₆ by isothermal annealing (in absence of any perturbation) below the anomaly at ~ 3.5 K [13]. This effect is one of the crucial probes in glasses when one follows how enthalpy of the system relaxes towards the equilibrium value during a long annealing at $T_a < T_g$. The glass is said to be "stabilized" if it really reaches this value. The lower is T_a , the longer the time needed to reach complete stabilization, so that these effects might be observed only not too far below T_g due to shorter relaxation times (more details are given in reference [13]). Figure 4b shows how " C_p " - the short pulse enthalpy susceptibility evolves with time spent at the same temperature $T = 2.92$ K for different $t_w = t_a$. It is a direct demonstration of the time dependence of the configurational component of the entropy. Although restricted to only three points (1,2,3 in fig.4b) it may be shown that " C_p " during the isothermal annealing at this temperature follows quasilogarithmic (or power law) time evolution, a reminiscence of the growth of the isothermal remanent

magnetization in SG. It looks like that in PF₆ the time dependence progressively disappears on reaching higher temperatures, just above the C_p anomaly [13].

3. Is there a glass transition at $T_g < T_p$?

The foregoing discussion was on aging experiments on DWs, and also for other glasses but performed near T_g where the transition is well established. The question of the occurrence of a glass transition at T_g at low T in DW is now addressed. Some models, based on elastic deformations of CDWs [14], give very detailed analysis of a glassy relaxation, but they did not specify any singular temperature below T_p . It is widely accepted that the freezing develops gradually and that the single particle (Peierls) gap is the highest barrier which is governing the activated dynamics of the complex glassy relaxation. However it seems to be very difficult to connect the "high" temperature behaviour with the low temperature ($T < 1$ K) relaxational behaviour with activation energies of 1-2 K (discussed above). Which is the best way to distinguish the gradual slowing down characteristic of a DW slush from a DW glass phase ?

In fact the very recent dielectric measurements [15] at low frequencies and at low temperature are the missing link between these different temperature regions. The low temperature experimental data of dielectric constant and specific heat of one CDW prototype system, TaS₃ and one SDW prototype system, PF₆, substantiate the separation into two distinct dynamical regions. On the one hand the real part of the dielectric constant in these DWs shows strong slowing down and points towards a "static" glass transition temperature ($T_g \sim 2$ K in PF₆ and $T_g \sim 13$ K in TaS₃). On the other hand the pronounced time dependent "specific heat" shows enormously increased time needed for achieving the TDE. The low-frequency dielectric response represents the primary, α , process in which the domains of correlated DW phase are getting stiffer (due to the disappearance of screening) but they still grow up [15]. The arrangement of this domains gives rise to a distribution of barrier height and at enough low temperature the motion over the high barriers is suppressed; "viscous flow" can no longer occur at a detectable rate and the glass transition "appears". The network of DW topological defects (dislocations, walls, etc.), coarsening in the freezing process, might give to the system another possibility to relax. This type of rearrangements involving the lower barriers gives rise to this very slow relaxational β process, i. e. the secondary process in the glassy state (there exists certain confusion in using α and β in the terminology of field of glasses) as has been detected in the enthalpy relaxation.

Fig. 5 - a) Variation of relation time τ in dielectric ($\square$) and energy relaxation ($\bullet$) measurements as a function of T^{-1} in PF₆. For dielectric relaxation the data $\tau = \nu^{-1}$ correspond to maxima in the real part of the dielectric constant for $\nu = \omega/2\pi$. Relaxation time for energy relaxation $\tau = \tau_e$ is this one at the thermodynamical equilibrium when aging effects are saturated [12]. When extrapolated, both relaxation processes merge at $T_g \sim 2$ K. b) Relaxation rates of o-terphenyl as given by different methods ; solid and dashed lines are guides for eye (taken from ref. 16).

We are now going to briefly discuss these results in the general frame of glassy transition. It is widely accepted that slow, secondary, β relaxation following an Arrhenius law at $T < T_g$ is a basic feature of the glass transition. In contrast to the fast α , the β process also persists below T_g . At higher temperatures the β process merges into the α one when its mean correlation time reaches that of the α

process. In this context we can propose the same scenario for SDWs as for CDWs [1,3,12,15] as there are no essential differences between DWs except that there is no lattice distortion in SDW.

The separation or bifurcation [16] between two different relaxation processes at low temperatures in PF₆ is clearly visible in figure 5 compared to o-terphenil as a prototype of supercooled liquids. If the measured dependence of relaxation time with T for PF₆ are both extrapolated, the cross-over between both processes would occur around 2 K, temperature we can tentatively define as the glassy transition temperature T_g [12]. This dynamical evidence together with a calorimetric one [13] shows a transition to a DW glass phase. The nature of this transition is very unique one as it concerns collective modes in the system which is essentially characterized by electron Fermi surface. Even if it shows all characteristics of the supercooled liquid [13] however we are dealing with a solid with a well established long range DW order. Although it is possible to introduce generalized viscosity through the viscosity of the "liquid of normal electrons" as Mc Millan had proposed (see in ref.14) and describe a glass formation as merely a result of an increase in viscosity, it is preferable to accept a more general description of glass formation in terms of "non-lattice" defects which diffuse both locally and through the structure of a solid, maintaining a spatially and temporally random distribution [17]. Moreover it is a new and promising theoretical model in which our earlier propositions that the defects in DW superstructure might be at the origin of long relaxational dynamics at low temperatures finds a fertile soil for further detailed considerations.

4. Conclusion

The very unique features of DW systems overlap with similar properties of very diverse set of glassy materials ranging from spin glasses to polymers, but they also show some particularities which might help for a better understanding of glassy behaviour. DW system presents a very good model system for reduced dimensionality, competing time and energy scales. It will be of great interest to classify DWs regarding their dynamical behaviour and to find out the relation between the "fragility" [1,12,13] of the system, the intensity of underlying electron-phonon interactions and screening phenomena. The pronounced change in dynamical behaviour in the form of cross-over from more "fragile" to "strong" glassy behaviour is an indication of more intensive freezing in processes [12]. As in the case of PF₆ there is no doubt on the underlying glass transition [12, 13], in the case of CDW systems the change of dimensionality should not be excluded [18].

We believe that through the electron-phonon interactions in DWs the nonlinear properties related to the pinning should be also affected by freezing processes on approaching the glass transition. Moreover there are experimental evidences in both SDW and CDW systems that this change occurs in the region of possible glass transition.

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