

## Bimodal Energy Relaxation in Quasi-One-Dimensional Compounds with a Commensurate Modulated Ground State

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We show that the low temperature ( $T < 0.5$  K) time dependent nonexponential energy relaxation of quasi-one-dimensional compounds strongly differs according to the nature of their modulated ground state. For incommensurate ground states, such as in  $(\text{TMTSF})_2\text{PF}_6$  the relaxation time distribution is homogeneously shifted to larger time when the duration of the heat input is increased, and exhibits, in addition, a scaling between the width and the position of the peak in the relaxation time distribution,  $w^2 \sim \ln(\tau_m)$ . For a commensurate ground state, as in  $(\text{TMTTF})_2\text{PF}_6$ , the relaxation time spectra show a bimodal character with a weight transfer between well separated slow and fast entities. Our interpretation is based on the dynamics of defects in the modulated structure, which depend crucially on the degree of commensurability.

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Nonexponential relaxation is the fingerprint of disorder in a system subject to an external perturbation [1]. It is the consequence of a broad distribution of relaxation times. The question of determining the nature and spatial extent of correlated objects responsible for slow dynamics in spin glasses and glasses, has been debated for several decades. In spin glasses, the memory and chaos experiments [2] give information about excitations in real space. In glasses there is a consensus that structural relaxation occurs on correlated domains of a nanometer size [3]. In colloidal suspensions, a direct three dimensional (3D) imaging of the cooperative motion in structural relaxation has been obtained on micrometer scales [4]. A general framework for describing spatial and temporal heterogeneities in aging systems has been proposed in Ref. [5]. A new class of mesoscopic glass, with characteristic scales of micrometers, has been recognized among quasi-one-dimensional systems [6]. Heat relaxation at very low temperature  $T$ , below 0.5 K, in these systems, has been shown to be nonexponential and to exhibit aging [6], in which the entire wide spectrum of relaxation times is shifted to longer times with increasing duration of the very small heat perturbation. We suggest here, on the basis of heat relaxation experiments, that the formation of correlated objects in modulated quasi-1D systems, is qualitatively different in commensurate and incommensurate systems.

Quasi-1D systems exhibit a variety of modulated electronic ground states at low temperature both in the charge channel, such as charge density wave (CDW), and in the spin channel, such as spin density wave (SDW), spin-Peierls (SP), or antiferromagnetic ground state. Extensive investigations of the low- $T$  thermodynamical properties [6–9] have shown that all of these systems demonstrate well-known universal features of glasses regardless of the actual ground state. This involves an extra contribution to the specific heat  $C_p$  coming from low energy excitations,

and nonexponential heat relaxation dynamics for  $T < 0.5$  K ( $T$ -range dominated by these excitations). “Aging” effects are also involved, where heat relaxation and, correspondingly,  $C_p$  depend on the duration of a small heat perturbation (a few mK) [6–8]. Extremely long relaxation times (up to  $10^4$  s) show that these excitations are only weakly coupled to the phonon heat bath [8], contrary to conventional glasses.

The origin of these excitations can be inferred from the low frequency dynamics of collective excitations in the charge channel. The low frequency dielectric response of CDW [10], SDW [11] which also has CDW component [12], all having a modulated charge density, is characterized by an overdamped (relaxational) mode slowing down with decreasing temperature. This has been recognized in the case of CDW and SDW (DW) as the sign of a glass transition at the level of the electronic superstructure. Freezing is naturally generated by screening effects and occurs if there are not enough free carriers to screen efficiently elastic DW phase deformations. Consequently, the characteristic scale of a DW glass is given by the phase coherence length, which is on the order of a  $\mu\text{m}$ . Below the glass transition temperature  $T_g$  the low frequency dynamics, and therefore the low energy excitations, are governed by the remaining degrees of freedom—topological or plastic deformations such as solitons, domain walls, or dislocation loops.

In this Letter we contrast two isostructural systems,  $(\text{TMTSF})_2\text{PF}_6$ , which has an incommensurate mixed SDW-CDW ground state below 12 K, and  $(\text{TMTTF})_2\text{PF}_6$ , which exhibits a charge order transition with a ferroelectric behavior at 70 K [13], and a spin-Peierls transition at 12 K, both being commensurate to the underlying lattice (in the following we use the notation SDW-PF<sub>6</sub> and SP-PF<sub>6</sub>, respectively). We will show how the degree of commensurability affects the very low- $T$  dynamics and discuss

these findings in view of the properties of solitonic excitations.

We have measured the low- $T$  heat capacity by the standard relaxation method. The system is first stabilized at a temperature  $T_0$ . Then small power is fed to the sample during a pumping time,  $t_p$ . The temperature is increased to the new, slightly higher value  $T_0 + \Delta T$  ( $\Delta T/T_0 < 0.05$ ). At  $t = t_p$  the power is switched off and heat relaxation from the sample to the cold source (towards equilibrium at  $T_0$ ) is recorded as a function of time. For all the CDW and SDW systems studied previously, below 1 K relaxation starts to deviate from the exponential on lowering  $T$  and also exhibits a strong dependence on  $t_p$  [6,7] (Fig. 1). A better characterization of nonexponential relaxation can be obtained by the relaxation rate  $S(t) = d(\Delta T/\Delta T_0)/d(\ln t)$ .  $\Delta T(t)/\Delta T_0$  can be written in terms of a distribution of relaxation times  $P(\ln \tau)$  as

$$\frac{\Delta T(t)}{\Delta T_0} = \int_{\ln \tau_0}^{\infty} P(\ln \tau) \exp(-t/\tau) d \ln \tau, \quad (1)$$

where  $\tau_0$  is the microscopic time. Since  $P(\ln \tau)$  varies slowly with  $\tau$  we replace the exponential by a step function, from which we deduce  $S(t) = P(\ln t)$  [14]. As in spin glasses there is a ‘‘homogeneous’’ broadening and shifting of the relaxation peak with  $t_p$  [see Fig. 1(b)]. However,

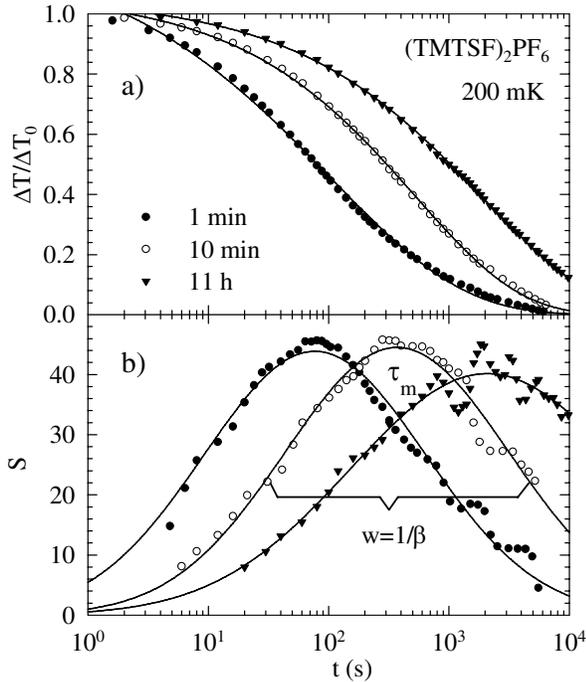


FIG. 1. *Homogeneous* broadening and shift of the heat relaxation with increasing  $t_p$  (aging) for SDW-PF<sub>6</sub>. (a) Relaxation  $\Delta T/\Delta T_0$  vs  $\log t$  with corresponding stretched exponential fit  $\exp(-t/\tau)^\beta$ , (b)  $S(t) = d(\Delta T/\Delta T_0)/d(\ln t)$  fitted to a Gaussian function  $G(\ln t)$  with a width  $w$ . The direct estimate of width at half height shown in (b) is 2.17 decades in agreement with  $1/\beta = 2.15$  and  $w = 2.1$ .

since our system eventually reaches thermodynamic equilibrium at  $T_0 + \Delta T$  for sufficiently long  $t_p$  [7], aging is then interrupted [15].

Nonexponential relaxation can be fitted by a ‘‘stretched exponential’’  $\Delta T/\Delta T_0 \sim \exp[-(t/\tau)^\beta]$  [6], while the relaxation rate  $S(t)$  can be fitted by a Gaussian distribution in  $\ln t$ :  $G(\ln t) = (1/\sqrt{2\pi w}) \exp(-\ln^2(t/\tau_m)/2w^2)$ , centered on  $\ln \tau_m$  and with a width  $w$ . Indeed, the logarithmic derivative of a stretched exponential  $d(\exp[-(t/\tau)^\beta])/d(\ln t)$  is almost a Gaussian with  $\tau_m \sim \tau$  and  $1/w \sim \beta$ , as shown in Fig. 1. The same  $w$  can also be extracted directly from  $S(t)$  curves as the width at half height.

While the stretched exponential has no known justification other than phenomenological [1,3], Castaing and Souletie [16] argued that a Gaussian distribution in  $\ln t$  can be justified in a framework that associates a hierarchical criterion and a usual scaling approach in the renormalization of distances. Similar to turbulence, they use a cascade of events to relate the macroscopic and microscopic scales. After iterating the renormalization group, dynamical scaling takes the form  $\tau/\tau_0 \sim (\xi/\xi_0)^z$ , where  $z$  is the dynamical exponent. The time scale distributions are log-normal:  $P(\ln \tau) \equiv G(\ln t)$  is Gaussian. The variance  $w^2$  scales with the most probable value  $\ln(t/\tau_m)$  [17] following the central limit theorem. It is demonstrated in Fig. 2 for SDW-PF<sub>6</sub> in thermodynamical equilibrium [9] for three temperatures chosen below 0.5 K. This immediately yields

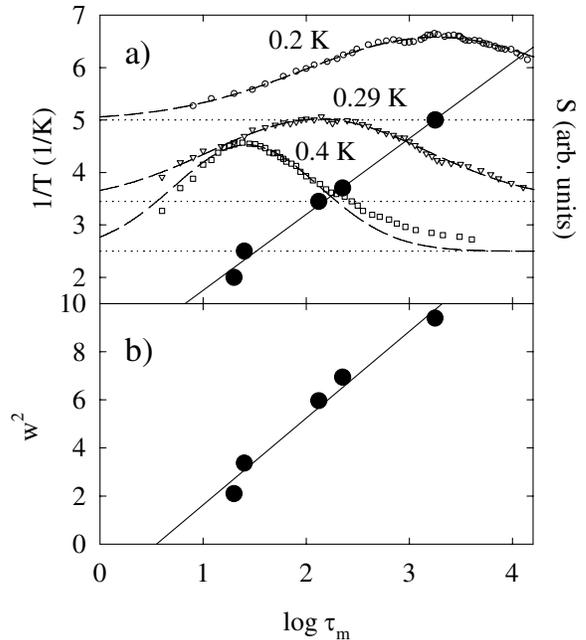


FIG. 2. (a) An ‘‘inverted’’ Arrhenius plot,  $1/T$  vs  $\log \tau_m$ , obtained for relaxations in thermodynamical equilibrium ( $\tau_m = \tau_{eq}$ ) of SDW-PF<sub>6</sub>. Relaxation rates and their fits are only shown for three selected temperatures among five. (b) The  $w^2 \sim \ln \tau_m$  scaling is well obeyed as expected from the central limit theorem. The activation energy is  $E_a = 1.7$  K.

the temperature dependence of the stretched exponential exponent  $\beta(T) \sim \sqrt{T}$ , as  $\beta \sim 1/w \sim 1/\sqrt{\ln\tau_m}$  [Fig. 2(b)], so that  $\ln\tau_m \sim 1/T$  indicates a thermally activated process with activation energy  $E_a = 1.7$  K. At this point we do not intend to go deeper into the different models related to  $\beta(T)$  for  $T \rightarrow 0$  (see Ref. [6] and references therein). We stress that the  $w^2 \sim \ln\tau_m$  scaling is quite convincing in the range of interest, and also for TaS<sub>3</sub>, a prototype CDW system, for which as well as for SDW-PF<sub>6</sub> a glass transition has been found at higher  $T$  [10].

However, in the case of SP-PF<sub>6</sub> [9] heat relaxation, while still nonexponential, exhibits quite different properties. Instead of the homogeneous broadening and shift of the spectra of SDW-PF<sub>6</sub> as in real aging effects, SP-PF<sub>6</sub> demonstrates “discrete bands” of relaxation times. Their distributions are narrower and the relaxation times are smaller than in SDW-PF<sub>6</sub> (i.e., saturation of aging is reached within a few tens of minutes as compared to days in the first system at a similar  $T$ ). Figure 3 shows a bimodal redistribution of the relaxation spectrum indicating that heat perturbation modifies different parts of the spectrum in contrast to the homogeneous shift of the entire spectrum as in Fig. 1.

Even in thermodynamical equilibrium the  $S(t)$  curves are not symmetric, indicating at least two different relaxation processes. However the total  $w$  (Fig. 4) can be obtained, but the variation  $w^2 \sim \ln\tau_m$  is very peculiar. We have successfully deconvoluted  $S(t)$  in two dynamically distinct Gaussian contributions, represented by dashed lines in Fig. 4(a). At higher  $T$ , the fast contribution plays the dominant role in the dynamics, but the relative weight of slow modes in the dynamics grows on decreasing the temperature. A similar behavior occurs at a fixed temperature if we change the duration  $t_p$  of the heat perturbation (Fig. 3). There is an evident weight transfer from one to the other subsystem as thermodynamic equilibrium is ap-

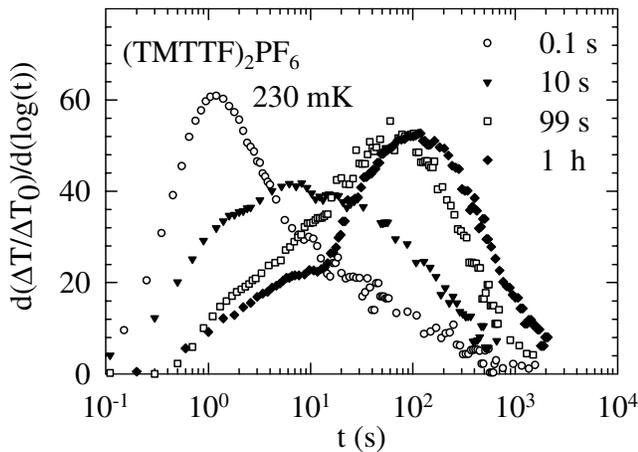


FIG. 3. *Bimodal* relaxation with redistribution of the spectral weight and saturation for  $t_{\text{eq}} \sim 10^2$  s for the spin-Peierls compound SP-PF<sub>6</sub>. The values of  $t_p$  are indicated on the figure.

proached. However, without the fast entities, there would be almost no response within  $10^2$ – $10^3$  seconds at the lowest  $T$ . The distribution of fast modes is pushed to  $10^3$  seconds at 85 mK, and the apparent activated behavior [Fig. 4(a)] turns into a saturation, indicating possible tunneling effects (not included in Fig. 4).

There are drastic consequences on the proper definition and determination of the specific heat  $C_p$  in these systems as it becomes strongly nonlinear [8]. From the deconvoluted entities in thermodynamic equilibrium [Fig. 4(a)], it is possible to calculate the corresponding  $C_p$ , fast and slow. Their participation changes progressively from approximately 100% for the fast modes at  $\sim 650$  mK to almost 90% for the slow modes below 400 mK.

It appears that the incommensurate CDW compound o-TaS<sub>3</sub> shares all its properties related with the shift of the dynamics with SDW-PF<sub>6</sub>. Both are nominally *incommensurate* systems. On the other hand, (TMTTF)<sub>2</sub>Br shares its multimodal dynamics properties with SP-PF<sub>6</sub> [9]. (TMTTF)<sub>2</sub>Br being the brother compound of SP-PF<sub>6</sub> is a *commensurate* antiferromagnet. We conclude our Letter by proposing an explanation to these distinctly different dynamics. The models generalizing Refs. [18–20] are investigated in more detail in Ref. [21].

As proposed by Larkin [18] and Ovchinnikov [19], the local deformations of the DW in the strong pinning limit are bisolitons, obtained by minimizing the elastic and

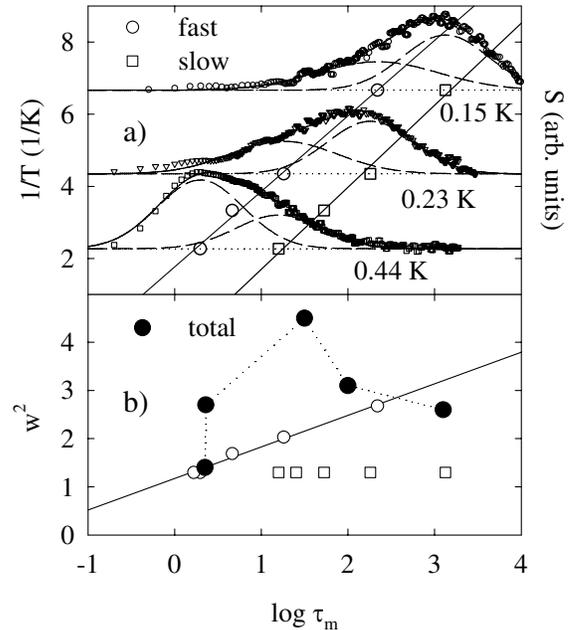


FIG. 4. (a) An inverted Arrhenius plot,  $1/T$  vs  $\log\tau_m$ , obtained for the relaxations in thermodynamical equilibrium of the spin-Peierls compound SP-PF<sub>6</sub>, together with a representation of corresponding relaxation rates for slow and fast processes and their fits, with  $E_{a,s} = E_{a,f} = 1.0$  K (b) The  $w^2 \sim \ln\tau_m$  scaling does not work for the total relaxation, however, it might work for each deconvoluted process.

pinning energies, and characterized by a ground state at energy  $E_0$ , separated from another state at energy  $E_0 + \Delta E$  by a “bounce” state at energy  $E_0 + \Delta V$ , therefore defining an effective two-level system. As a qualitative difference between commensurate and incommensurate systems [21], one has  $\Delta E = 0$  in the commensurate case [22] and  $\Delta E > 0$  in the incommensurate case, so that the populations of the effective two-level system does not couple to temperature variations in the commensurate case. We suggest here that, in addition, the degeneracy of the classical ground state in the commensurate case is lifted by quantum fluctuations that restore a finite heat response. The long time dynamics in the incommensurate case is due to collective effects, as suggested by the  $w^2 \sim \ln \tau_m$  scaling on Fig. 1, in agreement with Ref. [21]. The issue of the long time dynamics in the commensurate case, involving both quantum and collective effects, is mainly an open theoretical question.

To explain why the spectrum of relaxation time is bimodal in the commensurate case we note that experimental data suggest that in the commensurate system there exist two entities that relax with approximately the same energy barrier but with values of the “microscopic time” differing by 1 order of magnitude. Possible candidates for these two entities would be (i) the dipole solitonic excitations generated by the strong pinning impurities; and (ii) self-induced disorder due to  $2\pi$  solitons between microdomains separating the two spin-Peierls ground states. Alternatively, one may observe that SP-PF<sub>6</sub> has a charge gap  $\Delta_C \simeq 200$  K coexisting with a spin gap  $\Delta_S \simeq 20$  K, deduced from the spin-Peierls transition temperature from the mean field approximation. The coherence length in the charge channel  $\xi_C = \hbar v_F / \Delta_C \simeq 10a_0$  is thus much smaller than the coherence length in the spin channel  $\xi_S = \hbar v_F / \Delta_S \simeq 100a_0$  (where  $a_0$  is the lattice parameter and  $v_F$  the Fermi velocity). The two channels are weakly coupled so that the charge soliton, being smaller, relaxes faster than the spin soliton. The pinning potential and thus the energy barriers are identical in the two sectors so that the activation energies are identical but the microscopic times are different, in agreement with Fig. 4.

In conclusion we have shown manifestations of correlated objects interpreted as the collective dynamics of a disordered soliton lattice inherent to the modulated electronic ground state of DW. We demonstrated that a simple scaling feature of the parameters of the relaxation time distribution is well obeyed for the homogeneously broadened response for incommensurate systems. By contrast the heat response of commensurate systems is bimodal. We stress that our results should be also compared to other

experiments on the dynamical heterogeneity in the relaxations of supercooled liquids or spin glasses [23–25], and to the case of bimodal relaxation [26] observed in a fragile glass former at the approach of a glass transition. However, the microscopic picture is different, in spite of a similar phenomenology.

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