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Irreversibility and nonequilibrium dynamics in the pinned charge-density wave

D. M. Duggan, T. W. Jing, and N. P. Ong
Department of Physics, University of Southern California, Los Angeles, California 90089-0484

P. A. Lee
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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In the pinned state the charge-density wave displays irreversibility and nonequilibrium dynamics of an unusual nature as the applied voltage V is cycled. Relaxation from unstable states terminate at end points. In the process of depinning, the charge-density wave traverses a wide spectrum of time scales. The close relation of the time scales to the pulse-memory effect and ac dielectric constant is discussed.

The relaxation of disordered condensed systems ("glassy relaxation") towards equilibrium states has been a subject of great interest in recent years.[1] In systems as different as disordered dielectrics, polymers, spin glasses, and random-field magnets, logarithmic time or "stretched-exponential" time dependence of the relaxing observable Q are frequently encountered. In many models[2] the time dependence results from a continuous distribution of relaxation times. In a more recent theory[3] the stretched-exponential dependence

$$Q(t) = Q_0 \exp[-(t/t_0)^{\beta}] \quad (0 < \beta < 1) \tag{1}$$

is derived from a hierarchy of levels, whereby the relaxation of the $(n+1)$st level is constrained by the relaxation of the n th level.

A system that is receiving increased attention from the viewpoint of "glassy relaxation" is the pinned deformable charge-density wave (CDW) interacting with weak impurities.[4,5] In a class of quasi-one-dimensional compounds[6] typified by $NbSe_3$, TaS_3, and $K_{0.3}MoO_3$ the CDW condensate can be depinned when the applied electric field E exceeds a threshold E_T. In the *pinned* state the CDW has many configurations which are almost degenerate in energy because of its deformability and the large number of internal degrees of freedom.[5] In the process of pinning and depinning the system is forced to visit a succession of these states. Transitions between these configurations may occur on time scales for exceeding experimental times. Such a situation leads to irreversibilty and nonequilibrium dynamics in the pinned configuration. We show in this paper that the CDW (unlike many disordered systems) can always be prepared reproducibly in a stable state. It can subsequently be made unstable and studied, by simply changing the applied dc voltage V. The relaxation process, although rich and varied follows a clear, reproducible pattern. We demonstrate the existence of a line of stable points with an interesting structure. The approach of the system towards this stable line is via a unique *interrupted* relaxation process. We also show the existence of a very large range of relaxation times τ which is continuously accessed by the pinned CDW as E is increased from zero towards E_T. The effect of E on τ has also been studied recently by Mihaly, Janossy, and Kriza[7] in TaS_3. The pulse-memory effect first seen by Gill[8] is shown to be a direct consequence of this distribution of τ.

As shown by Gill[9] the differential resistance R in these CDW compounds has an unusual dependence on the electrical history. The R-V curves are hysteretic, with the zero field R depending on the current direction when V last crossed the threshold V_T. The inset of Fig. 1 shows a typical hysteretic loop obtianed by cycling V slowly (5 mV/min) so that it crosses threshold V_T for both current directions. As long as V exceeds V_T in both directions the *same* loop is traced out in each cycle. (The dashed lines in the inset show the bowing due to Joule heating.) By halting the voltage ramp at selected points we find that the region bounded by the loop is rich with structure, displaying well-defined regions of stable and unstable points. Some of these features are shown in the main panel of Fig. 1. Initially the CDW is pinned by reducing V below the threshold V_T (path 1-2). The system is stable everywhere along 1-2 and moves reversibly (1-2-3) as long as V is positive. We call this stable state A. Instability sets in when V changes sign. For example, when V is held fixed at 7 the system relaxes downwards (R decreases). However, instead of proceeding to the line 4-5 the relaxation stops at 8 (which we call a stable end point). If V is next increased to zero the system remains stable until V crosses zero, whereupon it again becomes unstable, this time (8-9) relaxing *upwards*. Corresponding to

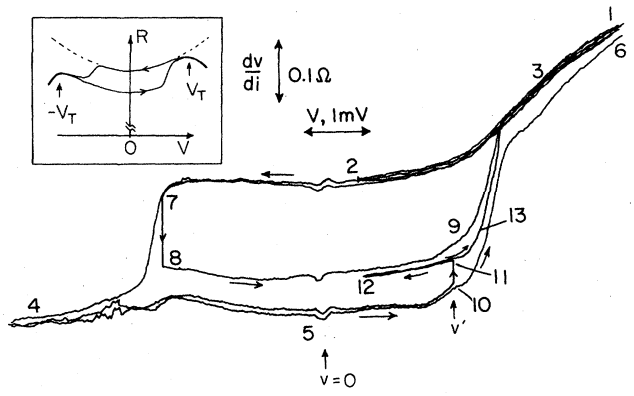

FIG. 1. Hysteresis traces of the differential resistance R ($= dV/dI$) vs the applied voltage V in $NbSe_3$ at 29.6 K. The vertical lines are nonequilibrium relaxations of the system with V held constant. Threshold voltage (7 mV) is outside the range of the drawing. The overall size of the hysteresis (0.2 Ω) is 0.4% of the total dc resistance. A schematic of the full hysteresis including threshold is shown in inset.

state A there exists the stable state B which is accessed from the left (V initially large and negative). The system is stable in B if V is negative (4-5). Relaxation out of state B occurs when V is made positive (10-11).

From the foregoing evidence we deduce the existence of two stable states A and B which are accessed when the CDW is pinned from an initially sliding state. (Interestingly, this is the only convenient way to reach the stable states. Other routes such as changing T lead to unstable states which are very remote from A and B.) The freshly pinned CDW is stable in these states as long as the field does not change direction. When V changes sign, relaxation towards the other state (say from A to B) occurs on a time scale which is very sensitive to E and T. The relaxation is, however, *interrupted* when the trajectory reaches the stable end points. The structure near these stable points is interesting. In Fig. 1 V is held at the value V' while the system relaxes from 10 to 11. If V is now reduced the system remains stable between 11 and 12. On restoring V to V' the system retraces its path, revisiting the point 11 before escaping to 13 (as V is further increased). In contrast, if the point 11 is approached along a path starting from state A via the point 8, the path veers away from 11 before V attains the value V', demonstrating that the system is unstable when V is positive. We deduce from this that the R-V plane actually consists of two sheets. Trajectories originating from the left end points such as 8 are stable (unstable) when V is negative (positive) and are confined to the upper sheet. States originating from the right (11) travel on the lower sheet, and have the opposite stability conditions.

A set of trajectories emanating from left end points is shown in Fig. 2 (traces 7,9,11,13). For each trace the system is "prepared" by depinning the CDW with a large, positive V. Then it is led along the upper curve (4,6,8) and allowed to relax vertically at fixed negative V. After the relaxation stops at the end point the system is pulled to positive V and the next trace executed. Note that the coordinates of the stable end points depend on the value V is held at. The sharp corners at the left of the drawing are in fact the *locus* of the end points. An alternate way to trace out the locus is shown by the staircase structure on the right. After relaxation at a fixed V is complete, V is slightly incremented, and the system is allowed to relax at the new V.

Irreversibility. The overall impression obtained in these studies is the sense of irreversibility when V is cycled. For example, if the relaxation 7-8 in Fig. 1 is aborted midway by reducing the magnitude of V the system stays frozen as long as V is to the right of the locus. As soon as V is restored the relaxation resumes until 8 is reached. Once such relaxations are initiated it is not possible to reverse the process or to recover the original state. Thus, the state 7 in Fig. 1 cannot be accessed again unless the CDW is completely depinned in the positive direction and the curve 1-2-7 retraced. Irreversibility is also strongly expressed in the unusual structure of the stability locus. Points on this locus can only be *approached* vertically (in the R-V representation), whereas trajectories leading away from the points are always horizontal. This restriction immediately implies the staircase structure seen in Fig. 2. Since every stable end point shares these constraints it is not possible to physically move from one stable point to an adjacent one without leaving the locus itself. In other words, the locus is a collection of points in the R-V plane which, though densely packed together, cannot be traced out continuously by adjusting a physical parameter (here V). On comparing Figs. 1 and 2 we see that the position of the locus relative to the threshold field is strongly T dependent. At low T complete relaxation occurs long before V reaches V_T, while at higher T (Fig. 2) complete relaxation occurs just before V reaches V_T.

Dynamics. In contrast with the complicated structure of the R-V plane the dynamics is quite simply described. Using a fast digitizer we captured the variation of R versus time t during the relaxation process (Fig. 3, main panel). The R vs t curve shows two regimes: at early times R is almost t independent; at later times it follows a logarithmic behavior which is interrupted at a time defined as τ. The R

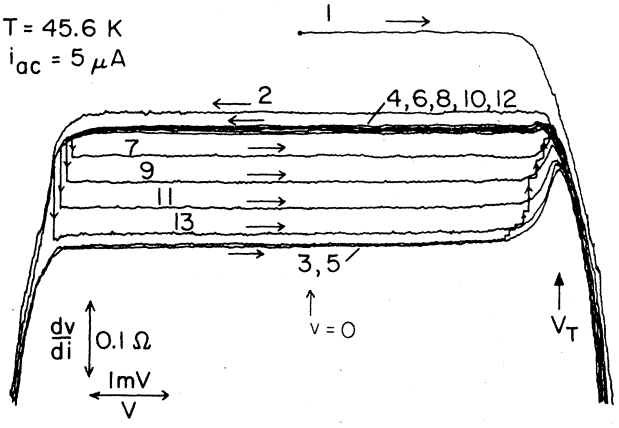

FIG. 2. Hysteresis traces of R vs V for $NbSe_3$ at 45.6 K. The locus of stable end points is generated in a staircase pattern on the right. The state 1 is the initial state right after T is raised to 45.6 K. Note that threshold $V_T = 2.7$ mV is exceeded near the end of the staircase structure. (See text.)

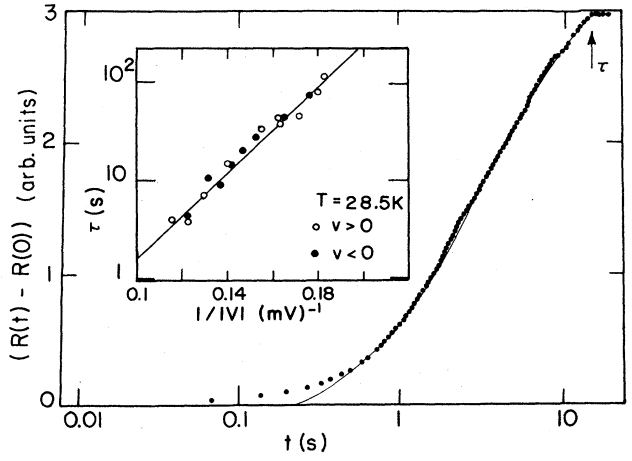

FIG. 3. Main panel: The relaxation of R at fixed V vs $\log_{10} t$ in $NbSe_3$ at 28.5 K. The data are direct digitizations of the lock-in amplifier output. The solid line through the data is a fit to Eq. (1). Logarithmic evolution does not set in until 1 s has elapsed. The relaxation is interrupted at a time τ which is V and T dependent. The variation of τ with $1/V$ is plotted in the inset for V of both signs. The fit to Eq. (2) gives $\tau_0 = 9.0$ ms, $A = 16.1$ V K/cm.

vs t data can also be fitted (for $t < \tau$) to the stretched-exponential form [Eq. (1)] with $t_0 = 3.93$ s and $\beta = 0.800$. Directly after V is frozen the system appears to pause briefly before undergoing relaxation. [This initial pause is not adequately described by Eq. (1); it is also responsible for the horizontal trajectories away from the stable end points described above.] By measuring τ for various T and V we find empirically that it obeys

$$\tau(T,E) = \tau_0 \exp(A/TE) , \quad (2)$$

where A is a positive constant, i.e., τ is both field and temperature activated. The fit of the data at 28.5 K is shown in Fig. 3 (inset). The rather large value of A means that the CDW (starting in an unstable state) accesses an enormous range of time scales as V is increased from zero towards threshold (100 s to 10 μs in our studies).

A more direct measurement of τ is to exploit the response of the pinned CDW to voltage pulses. As found by Gill[8] the current response of the CDW to unipolar voltage pulses is as fast as allowed by the electronic circuitry. However, when pulses of opposite signs are applied the response is sluggish. This is often called the pulse-memory effect. In view of the R-V structure presented here, this effect may be seen to be a direct consequence of relaxation from unstable to stable states. In Fig. 1 the CDW pins and depins reversibly along curve 1-2 in response to a string of positive V pulses; i.e., it always enters and leaves the same stable state A. However, for a negative pulse, the CDW is forced to convert to the state B along a trajectory such as 7-8 (depending on the magnitude V of the new pulse). The sluggish response of the sample merely reflects the time τ of relaxation. (Hence the pulse-memory effect is a property of the *pinned* CDW.) Using a fast digitizer we have studied the current transients (Fig. 4, inset) as a function of V and T and verified that I is again an interrupted stretched exponential or logarithmic curve analogous to Fig. 3. The time τ can thus be read directly off the digitized trace. In Fig. 4 we show the verification of Eq. (2) over the time scales 3 ms to 4 μs for $NbSe_3$ and orthorhombic TaS_3.

Discussion. Some of the phenomena discribed here are reminiscent of those observed in spin-glass[10] and random-magnet systems.[11] Several classical models which incorporate the existence of multiple closely degenerate states separated by barriers are capable of describing the irreversibility and hysteresis. The T-activated behavior of τ and the logarithmic variation of R can be described in models[12] in which the barriers grow as the system advances in its configuration space. However, the abrupt interruption of the logarithmic decay appears to be unique to the present system. Clearly many questions remain. While it is natural to suppose that the hysteretic change in R is due to the normal carriers moving in different CDW configurations, we need to postulate a microscopic mechanism such as the existence of a screw dislocation (in the host lattice) which allows the sample to distinguish left from right. After that we still have to account for the peculiar double-sheet structure in the R-V plane, the unusual structure of the stability loci, and the existence of the large range of time scales implied by Eq. (2). The larger question of the connection between the strong T and E dependence of τ and its relation to depinning is also interesting. Although the two states A and B are most easily distinguished by observing R we note that the sign of R_A-R_B (i.e., the sense of rotation of the loop) is not intrinsic to the system. It can be changed by altering the contacts or by a thermal gradient. We have established that the sign is neither correlated with the growth direction of the sample nor determined by E-field cooling. What is intrinsic is the relaxation dynamics and measured time constant when the system evolves from A to B at fixed T. Altogether 26 samples of $NbSe_3$ and five samples of TaS_3 were studied.

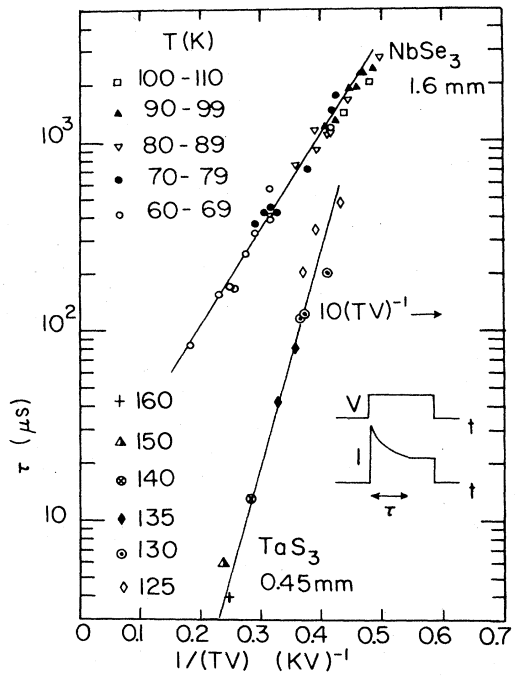

FIG. 4. The relaxation time τ measured by current transient response vs $1/(TV)$, where T is the temperature and V the voltage-pulse height. The fit to Eq. (2) gives $\tau_0 = 10.4$ μs, $A = 72.3$ V K/cm for $NbSe_3$ (upper line), and $\tau_0 = 6.7$ ns, $A = 5\,850$ V K/cm for TaS_3 (lower line). τ_0 and A are strongly sample dependent. The inset shows the applied voltage pulse and the transient (zero-suppressed) current response. Between measurements the samples are prepared by applying a large negative pulse.

Aside from the pulse-memory effect and the zero-field logarithmic-decay experiments, the work here may relate to recent studies of the ac response of the pinned CDW. The system switches between stable and unstable states each time the applied field changes sign. The relaxation from the unstable states during part of the ac cycle will induce a reactive current which can be shown to be capacitive in phase. (In the pulse-memory effect this phase relation corresponds to a current overshoot as drawn in the inset of Fig. 4.) It would be interesting to demonstrate that the low-frequency dielectric response recently reported[13-15] for TaS_3, $NbSe_3$, and $K_{0.3}MoO_3$ is in fact a manifestation of the relaxation processes described here in the frequency domain. The activated behavior of the mean-ac relaxation time seen[14,15] in $K_{0.3}MoO_3$ and TaS_3 is encouraging in this regard.

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