# Nonequilibrium Dynamics of Discrete Fluctuators in Charge-Density Waves in $NbSe_3$

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Individual two-state and multistate fluctuators were found in the broadband noise in the sliding charge-density-wave (CDW) state of small samples of $NbSe_3$. In the presence of dc currents, some multistate fluctuators violate detailed balance. Fluctuator properties show strong dependences on bias. As the CDW is cycled from sliding to pinned and back, it usually remembers which state of the fluctuator it is in, but some finite transition rates are found in the pinned CDW. Similar fluctuators persist in the presence of high-frequency ac bias.

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Charge-density-wave (CDW) materials in principle provide some of the simplest examples of systems for which randomness plays an essential role in the thermodynamic and transport properties [1]. The CDW is pinned by randomly placed impurities, each of which tries to dictate the local CDW phase. Since the CDW has finite stiffness, it cannot simultaneously minimize the energy at every pinning site. As with other systems combining such "frustration" with randomness, the CDW is expected to have many metastable configurations (MCs).

The Fukuyama-Lee-Rice (FLR) model [2], taking into account only the CDW phase, not its amplitude, predicts that the multiple metastable phase configurations of the pinned state [3] merge into a unique state when sufficient voltage is applied to depin the CDW into sliding conduction [4]. Studying the MCs can help reveal (among other things [5]) whether defects (e.g., dislocations) in the CDW, neglected in the FLR model, are important.

There are many signs of spontaneous fluctuations among the MCs in pinned CDWs. These signs include low-frequency internal friction, e.g., [6,7] and frequency-dependent ac conductivity [8], which correspond to elastic and electric dipole-moment fluctuations, respectively (via the fluctuation-dissipation theorem). Most relevant to this paper, in ultrasmall samples of *o*-$TaS_3$ discrete switching among different MCs has been observed in the pinned-state resistance [9].

Since low-frequency broadband noise (BBN) in transport properties has often been useful in probing the dynamics of disordered systems with many MCs, e.g., [10], BBN may shed light on the CDW's poorly understood MCs. Large BBN is routinely found in CDWs, but generally only in the *sliding* state.

Bhattacharya and co-workers [8,11] proposed that the BBN comes from quasiequilibrium fluctuations in the CDW configuration, with the bias current essentially probing preexisting fluctuations. Other explanations for the large BBN have been sought that are unrelated to the pinned-state metastability [12,13]. Some evidence supports Bhattacharya's picture, especially in $TaS_3$ [11,14]. The bias current, however, seems to play a role in creating other parts of the fluctuations, especially in $NbSe_3$ [12,15,16]. If the BBN is to be used as a tool to understand more about the CDW, then one must sort out to what extent it reflects the MCs available to the CDW vs reflecting its properties as a strongly driven nonlinear system [16].

In this Letter we show that discrete fluctuators are present in the BBN of the *sliding* state in $NbSe_3$. The multistate fluctuators violate detailed balance, indicating that the bias current plays a qualitatively important role in their dynamics. However, several results suggest that similar fluctuators, no doubt with simpler dynamics, exist in the pinned state, as in $TaS_3$ [9]. These results include tracking individual fluctuators between the sliding and pinned states as well as observations of discrete jumps in CDWs which are driven with ac bias which causes the CDW to oscillate less than about a half wavelength.

The undoped $NbSe_3$ crystals used in these experiments were grown by the Cornell group [17]. All detailed experiments presented here were made on a single five-probe bridge device [14] of $2.0\times0.7$ $\mu m^2$ cross section and 240 $\mu$m length for each of the four intercontact arms. (Four similar samples were studied. All showed individual discrete fluctuators very similar to those to be described here.) The $NbSe_3$ whisker was placed on a glass substrate, and held in place by drops of epoxy at each end (at least 1 mm from the nearest contact). The electrical contacts were then made by evaporating $\sim$3 $\mu$m of Sn through a physical mask. Each contact had $\sim$5 $\Omega$ resistance, and each arm had $\sim$320 $\Omega$ resistance at room temperature. Prior experiments on thicker samples with a *larger* ratio of contact resistance to bulk resistance showed that the various forms of BBN observed were bulk, not contact effects [15], a result that should hold better for the thin samples. The *I*-*V* curve of the sample showed clean transitions to the sliding states, typical for good $NbSe_3$ samples, with no noticeable hysteretic switching effects at 90 K.

In these small samples with dc bias, we find both large individual fluctuators and a background of BBN not resolved into individual fluctuators, as can be seen in Fig. 1(a). The large fluctuators give voltage vs time records with easily resolvable jumps. We call these random tele-

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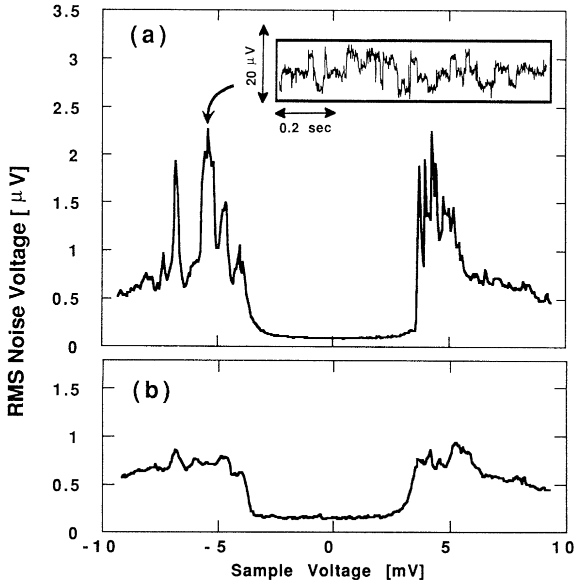

FIG. 1. rms noise vs average bias voltage $V_B$ (at constant current) of the sample. $T=90$ K, bandwidth 0.3-400 Hz. (a) A dc bias was used. For each large peak in the rms noise, discrete steplike fluctuations in $V(t)$ were found, as shown in the inset. (b) A 2 kHz offset square-wave current bias was used. The expectation of the bias voltage alternated between two values: +12 mV and the variable sample voltage $V_B$ at which the noise measurement was made. The voltage fluctuations were measured only at times when the $V_B$ was applied. The peaks were mostly suppressed but the background BBN survived.

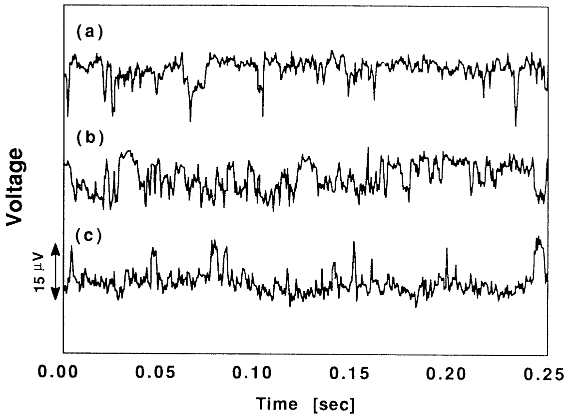

FIG. 2. Time traces of an individual fluctuator for slightly different successive bias currents: (a) $V_B/V_T=1.53$, (b) $V_B/V_T=1.58$, (c) $V_B/V_T=1.62$. Here the duty cycle is obviously strongly bias dependent, and the characteristic frequency (determined from power spectra) also changes almost a factor of 2 between traces (b) and (c). Each fluctuator has a unique bias-dependence signature.

graph signals (RTS) regardless of their detailed form and statistical properties.

An approximate lower bound on the size of each typical fluctuating region may be made using the extreme assumption that in one of the two MCs the CDW current is entirely suppressed over that volume. This lower bound comes out to be $\sim 10^{-11}$ cm$^3$, slightly smaller than a prior estimate ($\sim 2\times 10^{-10}$ cm$^3$) based on non-Gaussian statistics in larger samples [15]. The rough similarity to phase coherent volumes inferred directly from x-ray scattering [18] or from weak-pinning analyses [17] is interesting, as is the indication that finite-size effects are important. (These volumes are larger than the entire sample size used in some previous experiments on TaS$_3$ [9] but smaller than analogous volumes found in the BBN in TaS$_3$ [19].)

Macroscopic measurements on BBN in NbSe$_3$ have shown that audiofrequency bias switching between the two oppositely sliding states eliminates most but not all of the low-frequency noise, suggesting the presence of two different types of contributions to the BBN [15]. In the mesoscopic samples, applying such ac bias greatly reduced the large individual peaks but scarcely affected the remaining BBN magnitude in this frequency band, as shown in Fig. 1(b). Thus the more bias-sensitive component of the BBN consists of the large fluctuators.

As illustrated in Fig. 2, even small changes in bias (or temperature, as we shall describe elsewhere [19]) give large changes in the duty cycles and kinetics of the RTS, even though in macroscopic experiments the average spectrum is only weakly dependent on these parameters. Since different RTS are observed at even slightly different dc biases, an ordinary BBN experiment on NbSe$_3$ will not measure the *same* fluctuating modes that are present in the absence of bias current, at least for the part of the BBN comprised of large fluctuators. (Since the fluctuators in TaS$_3$, whether pinned [9] or sliding [19], show similar dependences, this conclusion applies to that material too.) The question then becomes to what extent the dynamics of these fluctuators statistically resemble dynamics present in equilibrium.

Whether the sliding-state BBN can be treated as a quasiequilibrium phenomenon can be directly answered by looking at three-state (or higher) RTS, since these can manifestly violate detailed balance [20]. The rates for switching among the different states violated detailed balance in each of the few clear multilevel RTS which we found, as shown in Fig. 3. Whether or not the MCs revealed by the sliding BBN are present in equilibrium, the actual dynamics observed in a typical BBN experiment on NbSe$_3$ is not describable by a quasiequilibrium model.

Although the configuration fluctuations which appear in the BBN have nonequilibrium dynamics, we found that the fluctuating MCs not only exist in the pinned state but also can have slow dynamics in the pinned state. The configuration must be measured in the sliding state, because its effects on the transport properties of the pinned state are too small. Since the macroscopic BBN retains its approximate form when the applied bias oscillates be-

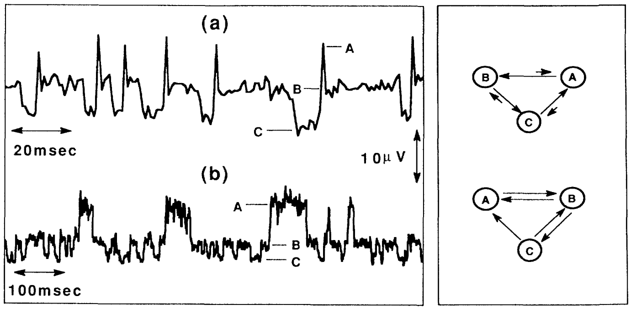

FIG. 3. Two small portions of long $\delta V(t)$ traces which consistently show violation of detailed balance. $T = 90$ K. (a) Obviously time-irreversible RTS at $V_B \approx 2V_T$, with the majority of transitions going $A \rightarrow C \rightarrow B \rightarrow A$, etc. (b) Three-level RTS at $V_B \approx 1.1V_T$. The total numbers of each type of transition were $A \rightarrow C$, 0; $C \rightarrow A$, 13; $A \rightarrow B$, 91; $B \rightarrow A$, 78; $B \rightarrow C$, 330. The $A \leftrightarrow C$ rates are well outside the statistical limits of detailed balance.

tween sliding and pinned [15], one expects that the individual RTS should remember their MCs as they go from the sliding state to the pinned state and back.

We picked several clearly resolvable two-state RTS, and measured the likelihood that each would return, after excursions into the pinned state, to the same sliding MC from whence it came. There was indeed a strong systematic tendency for each RTS to come back into the starting MC. However, an increasing number of transitions (i.e., returns to the other MC) were found as we increased the time spent in each excursion into the pinned state. Figure 4 shows a typical dependence of the probability of a transition on the time spent in the pinned state. Extrapolation to zero pinned time usually gave a finite transition fraction, indicating that some of the transitions are caused by the bias-switching process itself, as expected from the effects of bias switching on the elastic properties [7].

Thus even in the pinned state transitions occur spontaneously between the same MCs which give BBN in the sliding state. Since we know the transition probabilities as functions of time in the pinned state, we can extract transition rates. For all of the observed RTS, these rates were significantly less (typically 1 or 2 orders of magnitude less) than the rates in the sliding state. Although we observed several RTS in experiments of this type, for each one we found that only one direction of transition had a rate measurably above zero in the pinned state. Since, even within the pinned state, changing the bias by a small amount changes the duty cycle of each RTS dramatically [9,19], such a result is to be expected.

Since phase-slip processes at macroscopic heterogeneities (e.g., contacts) have been suggested as the origin of the BBN in $NbSe_3$ [12], we would like to see what the mesoscopic fluctuations in $NbSe_3$ look like in the absence of phase-slip processes. Here we distinguish between topological defects which can exist and have MCs in a static CDW and the phase-slip processes which occur at those defects as phase fronts move relative to each other in a driven CDW.

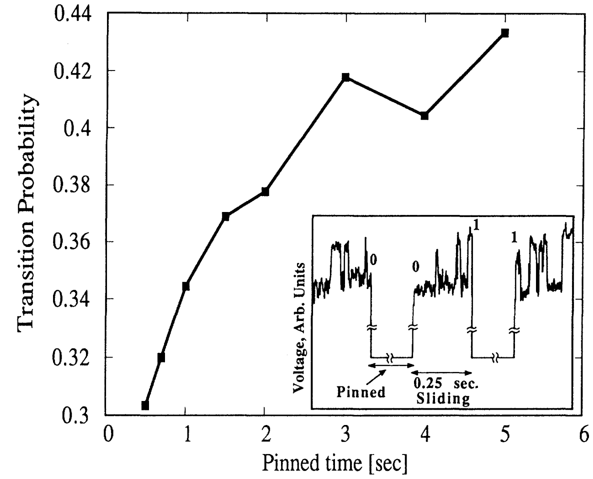

FIG. 4. Transition probability of a two-state RTS vs time spent in the pinned state. $V_b$ was alternately switched between a sliding state, in which the RTS was measurable, and a pinned state ($V_b = 0$). During the 0.25 s sliding periods, the RTS had a 56% duty cycle and characteristic times of about 0.03 s. For each pinned period the level (0 or 1) of the random telegraph was determined just before and after the pinned period. We interlaced excursions of different lengths, collecting their statistics separately, to avoid any effects of drifts. $T = 90$ K.

Macroscopic experiments on both $TaS_3$ [14] and $NbSe_3$ [15] have shown that low-frequency BBN can be found with no dc current when an ac bias is applied. This random-rectification ("vector") noise has been shown to arise in the bulk, not the contacts [14,15]. In $NbSe_3$, these macroscopic experiments showed that, although most low-frequency BBN is eliminated by above-threshold ac bias with frequency ($f_B$) in the audio range, when $f_B$ was increased to about 1 MHz, the "vector symmetry" component of the BBN was similar to the BBN obtained with dc bias [15].

We have measured BBN in mesoscopic samples with applied 1 MHz ac bias as low as $0.9V_T$, in experiments to be described in more detail elsewhere. Discrete steps can also be discerned in this BBN, although under these conditions the CDW oscillates only about 0.23 of its wavelengths from its equilibrium position, based on the dielectric constant [11] and the CDW charge density [12]. These results, like the pinned-state relaxations, suggest that driven phase-slip processes are not necessary to drive the CDW among its MCs.

In conclusion, the CDW obviously can find various MCs shared by the pinned and sliding states. These MCs apparently require the presence of defects in the CDW phase configuration [4]. Some defects must be generated as the CDW starts to slide [21], and some may also be present in thermal equilibrium [22].

Taken as a whole, our experiments suggest that the configuration fluctuations in the pinned state are similar to the fluctuations giving the BBN in the sliding state. Some of the same configurational changes probed in the sliding state BBN also occur slowly in the pinned state. The BBN measurements with high-frequency bias show that configurational fluctuations occur even in the absence of net dc current. It is most likely that these are essentially the same as the configurational fluctuations in the pinned state.

The large component of the BBN consisting of the resolved fluctuators is not a direct probe of those equilibrium fluctuations. The actual RTS found at any particular sliding bias are not ones which have two non-negligible transition rates in the pinned state. If most configurational changes have an associated electric dipole moment, it is not surprising that particular configurational degrees of freedom only show quasiequilibrium fluctuations over a narrow range of bias. Since the response to a changed bias is not instantaneous, for high enough frequencies of ac bias the low-frequency CDW configuration modes see something like an average effective field.

Equilibrium fluctuations, however, cannot violate detailed balance, unlike the constituents of the BBN in $NbSe_3$. Thus an effective field treatment cannot give the whole story for the BBN with dc bias. Detailed balance violations might arise, for example, in a model in which CDW dislocations move systematically in an electric field.

It has been suggested [23] that fluctuators observed in steady state may be qualitatively similar to modes involved in macroscopic current-driven hysteretic switches, except that the steady-state fluctuators have appreciable thermal transition rates. Our observation of individual fluctuators for which the thermal and current-driven dynamics compete not so bias sensitive comes from still smaller fluctuators, for which thermal rates apparently dominate the current-driven rates.

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