Charge-density-wave surface phase slips and noncontact nanofriction

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Bulk electrical dissipation caused by charge-density-wave (CDW) depinning and sliding is a classic subject. We present a local, nanoscale mechanism describing the occurrence of mechanical dissipation peaks in the dynamics of an atomic force microscope tip oscillating above the surface of a CDW material. Local surface 2π slips of the CDW phase are predicted to take place, giving rise to mechanical hysteresis and large dissipation at discrete tip surface distances. The results of our static and dynamic numerical simulations are believed to be relevant to recent experiments on $NbSe_2$; other candidate systems in which similar effects should be observable are also discussed.

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Charge-density waves (CDWs) are static modulations of small amplitude and generally incommensurate periodicities that occur in the electron density distribution and in the lattice positions of a variety of materials [1]. They may be generated either by an exchange-driven instability of a metallic Fermi surface [2], or by a lattice-dynamical instability leading to a static periodic lattice distortion (PLD), which may equivalently be driven by electrons near the Fermi [3,4] energy or just by anharmonicity [5]. A CDW superstructure, characterized by amplitude ρ_0 and phase $\phi(x)$ relative to the underlying crystal lattice, can be made to slide with transport of mass and charge and with energy dissipation under external perturbations and fields [1].

Phase slips in bulk CDWs/PLDs are involved in a variety of phenomena, including switching [6], current conversion at contacts [7], noise [8–10], and more. While these phenomena are now basic knowledge, there is to date no parallel work addressing the possibility to mechanically provoke CDW phase slips at a chosen local point. In this paper, we describe a two-dimensional model showing how a localized CDW/PLD phase slip may be provoked by external action of an atomic force microscope (AFM) tip outside a surface.

Experiments have for some time revealed the dissipative and frictional effects experienced by nanoprobes in contact with or near different surfaces, and considerable theoretical effort is being devoted to their understanding [11]. The development of ultrasensitive tools such as the "pendulum" AFM [12,13] offers a chance to investigate more delicate and intimate substrate properties. Near a CDW material, the tip oscillations may actuate, through van der Waals or electrostatic coupling, an electronic and atomic movement in the surface right under the tip, amounting in this case to coupling to the CDW order parameter. Due to the periodic nature of the CDW state, the coupled tip-CDW system has multiple solutions, characterized by a different winding number (a topological property), which differ by a local phase slip, and they correspond to different energy branches. At the precise tip-surface distance where the two branches cross, the system will jump from one to the other injecting a local 2π phase slip, and the corresponding hysteresis cycle will reflect directly as a mechanical dissipation, persisting even at low tip oscillation frequencies. This scenario and these results are believed to represent closely what is going on in recent experiments on the CDW material $NbSe_2$ [14].

I. THE MODEL

Irrespective of the microscopic mechanism that generated it, we introduce the CDW as a periodic modulation of the ion and electron density ρ, of the form $\Delta\rho(\mathbf{r}) = \rho_0 \cos(\mathbf{Q}\cdot\mathbf{r} + \phi_0)$, where ρ_0 is the amplitude, $\lambda \sim 2\pi Q^{-1}$ is the characteristic wavelength, and ϕ_0 is an initially constant phase, fixed by some faraway agent. We wish to study the effect of a localized perturbation represented by a weakly interacting and slowly oscillating nano or mesoscopic-sized probe hovering above the surface, acting on a length scale σ similar to the CDW wavelength, $\sigma \sim \lambda$. In the past, uniform perturbations such as external electric fields, or pointlike perturbations such as pinning defects, have been studied [1,15–17], describing global CDW dynamical sliding or local static CDW pinning. To address the problem of local CDW dynamics, we now go beyond the straight one-dimensional approximations commonly used in the past.

As in the standard Fukuyama-Lee-Rice model [15,16], we treat the CDW at the Ginzburg-Landau level as a classical elastic medium, where the CDW modulation is described by a static space-dependent (and, later, time-dependent) order parameter $\Delta\rho(\mathbf{r}) = A(\mathbf{r})\cos[\mathbf{Q}\cdot\mathbf{r} + \phi(\mathbf{r})]$. The unperturbed CDW has constant $A(\mathbf{r}) = \rho_0$ and $\phi(\mathbf{r}) = \phi_0$, and the free energy reads

$$\mathcal{F}_0[\psi(\mathbf{r})] = \int [-2f_0|\psi(\mathbf{r})|^2 + f_0|\psi(\mathbf{r})|^4 + \kappa|\nabla\psi(\mathbf{r})|^2]d\mathbf{r}, \tag{1}$$

where $\psi(\mathbf{r}) = A(\mathbf{r})e^{i\phi(\mathbf{r})}$, f_0 and κ are nonlinearity and stiffness real positive parameters, respectively, and a unidirectional CDW modulation has been assumed (three superposed modulations could be treated equally well). Next, the perturbation induced by an AFM tip is described as a potential $V(\mathbf{r})$ coupling to the order parameter

$$\mathcal{F}_V[\psi(\mathbf{r})] = \int V(\mathbf{r})\mathrm{Re}[\psi(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}]d\mathbf{r}. \tag{2}$$

Past studies of point impurities [17,18] assumed $V(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, one dimension, and coupling was restricted to the CDW phase only, but all of that is inadequate here. Indeed, if one considers a phase-only functional of the form

$$\mathcal{F}_\phi[\phi(\mathbf{r})] = \int \{\kappa|\nabla\phi(\mathbf{r})|^2 + V(\mathbf{r})\rho_0 \cos[\mathbf{Q}\cdot\mathbf{r} + \phi(\mathbf{r})]\} d\mathbf{r} \tag{3}$$

and minimizes it in one dimension, the result will be a linear behavior of $\phi(x)$ away from the impurity, unphysical. Therefore, it is mandatory to work in at least two dimensions, where the Laplacian can accommodate solutions that decay far from the perturbation. Moreover, the nature of the phase, defined modulo 2π, implies that, given some boundary conditions, the solution is not uniquely defined unless we also specify the total variation of ϕ. Assuming the phase to have the unperturbed value ϕ_0 far from the perturbation, we can define the *winding number* N

$$N = \frac{1}{2\pi}\int \nabla\phi(\mathbf{r}) dx, \tag{4}$$

taken along the CDW direction $\mathbf{Q}$. The winding number N is needed to fully specify a solution. However, this procedure leads to a problem of the phase-only approximation (3): any change in the winding number along the $\mathbf{Q}$ direction will reflect itself in the whole perpendicular direction, thus unphysically raising the energy of such a solution. For a physically sensible result, we need to involve the amplitude degree of freedom, which will allow for the presence of dislocations and for local changes in the winding number. Lastly, we require an extended perturbation since a point potential can only adjust the order parameter at a single point, therefore missing the extended information about the winding number and ultimately failing to produce a localized phase slip in the absence of external strains on the system. We will therefore consider $V(\mathbf{r})$ with a finite width σ of the order of the wavelength λ, and minimize the total phase and amplitude-dependent free energy $\mathcal{F} = \mathcal{F}_0 + \mathcal{F}_V$ given a specific shape of $V(\mathbf{r})$. The final result is expected to be similar to what was previously considered in the wider context of phase slip [17] and more specifically in the case of localized phase-slip centers [19,20]. Namely, the local strain induced by the perturbation on the phase will reduce the order-parameter amplitude, to the point where a local phase-slip event becomes possible. In more than one dimension, the boundary between areas with a different winding number will be marked by structures such as *vortices*.

From this preliminary analysis, we can now anticipate that, as the tip approaches the surface, increasing the strength of $V(\mathbf{r})$, it might reach points where the energies of solutions with different winding numbers cross. At these points, the transition between successive winding-number manifolds would not be continuous, due to the barrier required to create the vortices. As a result, time-dependent oscillations of the tip around these locations would generally occur with hysteresis and, ultimately, mechanical dissipation despite low oscillation frequencies.

II. SIMULATIONS

To verify the proposed mechanism, we performed numerical simulations of the tip-CDW surface model, restricted to two dimensions assuming that all effects will heal out below the surface (reasonable in a layer compound). To mimic the tip potential, we integrate a van der Waals potential C/r^6 over a conical shape at distance d from the surface. The result can be reasonably approximated in the main area under the tip as a Lorentzian,

$$V_d(\mathbf{r}) = \frac{V_d^0}{\mathbf{r}^2 + \sigma_d^2}, \tag{5}$$

where $\mathbf{r}$ is the in-plane distance from the tip central axis, and the parameters scale like $V_d^0 = \bar{V}/d$ and $\sigma_d = \bar{\sigma} d^2$. While this shape and dependence are not exact, they are good enough for our purposes, especially since the final qualitative results are not strongly dependent on the exact perturbation.

To minimize the total free energy $\mathcal{F} = \mathcal{F}_0 + \mathcal{F}_V$, we discretize the complex order parameter ψ on a square grid of points with a spacing much smaller than the characteristic wavelength of the CDW (and fine enough to avoid discretization artifacts), and we impose a constant boundary condition ψ_0 on the sides perpendicular to $\mathbf{Q}$, while setting periodic boundary conditions in the direction parallel to $\mathbf{Q}$ to allow for possible phase jumps [21]. The minimization is carried out with a standard conjugated gradients algorithm [22]. Without aiming at a numerically realistic representation of any experimental system, we use reasonable order-of-magnitude estimates of the system parameters, which help us build a clear if qualitative portrait of the tip-induced CDW phase slip.

Figure 1 shows the charge density ρ, order parameter amplitude A, and phase ϕ for minima with different winding number N, for a noncontact (attractive) tip at different distances d. The winding number is calculated along the line passing through the point right below the tip (center of the simulation cell) according to Eq. (4), with $N = 0$ being the unperturbed case. As predicted, we see upon decreasing d through the first and successive critical distances d_{01}, d_{12}, etc. the appearance of a pair of vortices (with opposite rotation) for every unit increase of the winding number. These vortices are characterized by a suppression of the amplitude and a total change of the phase by 2π on a path around them, since they separate the phase-slippage center from the unaffected area far from the tip.

Since the solution with a given winding number lies in a local minimum, it is possible to use the minimization algorithm, for example by starting from a reasonable configuration, to find solutions in a certain subspace, even when that is not the global minimum for that given distance. This allows us to extend the calculation of the local free-energy minima in a given N subspace well beyond their crossing points, generating a family of free-energy curves of definite N as a function of the distance d. In Fig. 2 (solid lines), we show an example of two successive crossing points. We expect each crossing to give rise to a first-order transition, and thus to a hysteretic peak in the experimental dissipation trace. Of course, a more complex CDW configuration or different parameters could give rise to more and different peaks.

To demonstrate the phenomenon in full, we now extend our study to the tip-CDW dynamics. Toward that end, we carry out a simulated evolution generated by the time-dependent

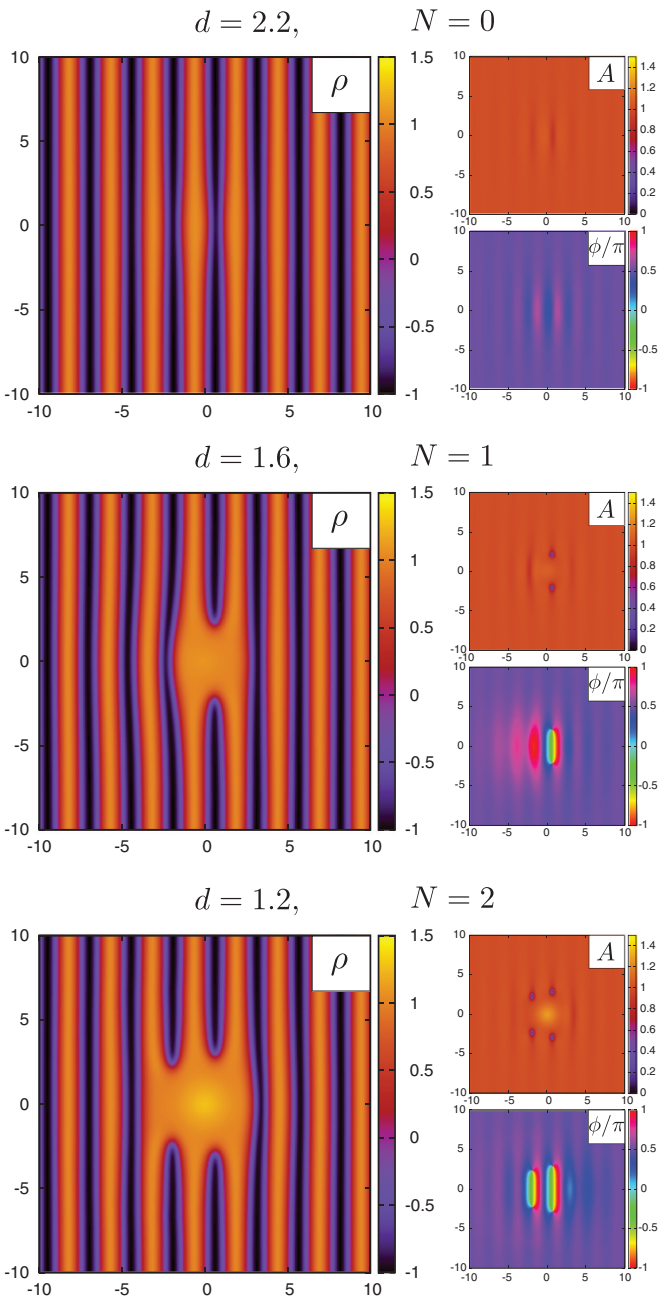

FIG. 1. (Color online) Charge density ρ, order parameter amplitude A, and phase ϕ portraits for minimal free-energy solutions with different winding number N and tip-surface distance d (in nm). Results from simulations on a 201×201 grid with parameters (see text) $f_0 = 2$ eV/nm, $\kappa = 0.2$ eV, $Q = 2.5$ nm^{-1}, $\bar{V} = -9.4$ eV nm, $\bar{\sigma} = 1.2$ nm^{-1}, and boundary conditions $\psi_0 = i$ (right and left sides).

Ginzburg-Landau equation [20],

$$-\Gamma \frac{\partial \psi}{\partial t} = \frac{\delta \mathcal{F}}{\delta \psi^*}, \tag{6}$$

which can be interpreted as an overdamped evolution of the order parameter toward the equilibrium position, with a damping coefficient Γ. The use of this equation is justified since the perturbation time scales are much longer than the ones typical of CDW motion, rendering inertial effects negligible.

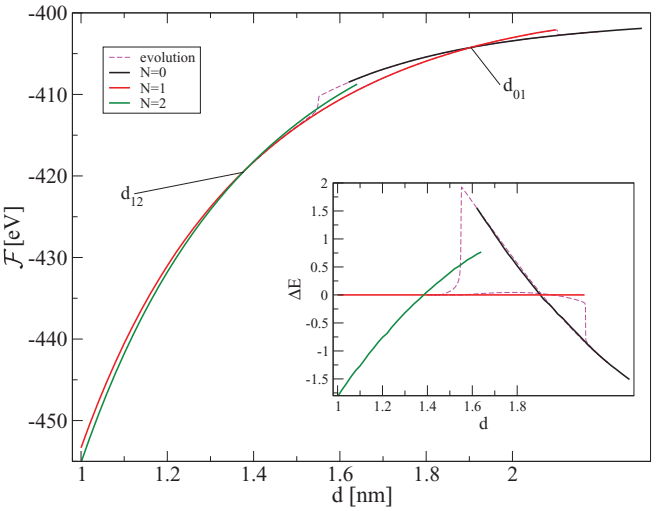

FIG. 2. (Color online) Minimal free energy $\mathcal{F}$ as a function of tip distance d for subspaces with different winding number N (full lines) and evolution of $\mathcal{F}$ during an oscillation with $d_0 = 1.8$ nm, $\bar{d} = 0.4$ nm, and $\omega = 6\times10^4$ Hz (other parameters are the same as Fig. 1). Inset: same data rescaled with respect to the $N = 1$ value to highlight their difference.

Integrating this equation (through a standard Runge-Kutta algorithm [22]), we compute the time evolution of the free energy, as shown by the dotted line in Fig. 2, for a tip performing a full oscillation perpendicular to the surface of the form $d(t) = d_0 + \bar{d}\cos(\omega t)$. The result [23] shows that in this effectively adiabatic evolution, the system is stuck in its winding-number manifold well beyond the crossing point, effectively realizing a hysteresis cycle. Figure 3 shows the force hysteresis for oscillations at different frequencies ω: the area of the cycles directly represents the dissipated energy per cycle W, given in the inset. It should be stressed here that what we calculated is in effect only a *maximal* hysteresis cycle.

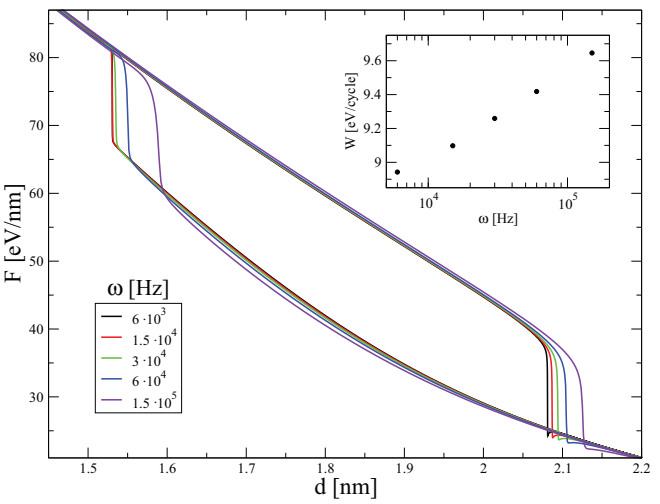

FIG. 3. (Color online) Force as a function of distance for evolutions with $d_0 = 1.8$ nm, $\bar{d} = 0.4$ nm, and different values of ω with a coefficient $\Gamma = 10^{-7}$ eV s. Inset: total work W as a function of oscillation frequency ω.

The actual size of the cycle, and thus of the total dissipated tip mechanical energy, is in principle smaller (and should in effect vanish in the limit of vanishing oscillation frequency) due to thermal fluctuations, which our treatment omits. However, as known in other cases, the large, mesoscopic size of the tip-surface mechanics generally makes the simple adiabatic description rather accurate, and the effective hysteresis only modestly frequency- and temperature-dependent. Moreover, considering that the experimental dissipation per cycle is of the order of half an eV, while the temperature is in the tens of K, even accounting for the barrier being smaller than the state separation, we estimate the probability of relevant thermal excitations spoiling all hysteretic effects in the ms span of a cycle to be negligible.

III. DISCUSSION AND CONCLUSIONS

We have shown that local surface CDW phase slips and vortex pairs can be introduced by the external potential of an approaching tip. In the context of macroscopic CDW conduction noise [1,9,10], the creation and movement of vortices has been invoked earlier in connection with phase slips near the CDW boundaries. In a broader context, our system can be placed in between these macroscopic situations and the simple models of defect pinning and phase slip [17] by a localized perturbation.

Experimentally, Langer *et al.* [14] recently reported AFM dissipation peaks appearing at discrete tip-surface distances above the CDW material $2H$-$NbSe_2$, qualitatively suggesting in a 1D model the injection of 2π phase slips. The present results describe at the minimal level a theory that can explain this type of phenomenon, connecting the phase slip to a vortex pair formation, and providing the time-dependent portrait of the injection process.

It would be of considerable interest in the future to explore this effect further in other systems with different characteristics. In insulating, quasi-one-dimensional CDW systems, the injected phase slip should also amount to the injection of a quantized, possibly fractional pairs of opposite charges [24]. In a spin density wave system, such as the chromium surface, a nonmagnetic tip would still couple to the accompanying CDW [25], where surface phase slips could be injected. In superconductors, the induction of single vortices over Pb thin film islands has been experimentally verified [26], and the feasibility of controlling single vortices through magnetic force microscopy (MFM) tips has been demonstrated [27]: it would be interesting to probe for dissipation peaks, as we have addressed above, induced by the MFM tip creation of vortex pairs in thin superconducting films.

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[23] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.245416 for a short movie representing the evolution of the charge density during a tip oscillation.
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