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CHARGE DENSITY WAVE POLARIZATION DYNAMICS

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CHARGE DENSITY WAVE POLARIZATION DYNAMICS

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Kentucky

By

Luis Alejandro Ladino Gaspar

Lexington, Kentucky

Director: Joseph W. Brill, Professor of the Department of Physics and Astronomy

Lexington, Kentucky

2008

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ABSTRACT OF DISSERTATION

We have studied the charge density wave (CDW) repolarization dynamics in blue bronze (K$_{0.3}$MoO$_3$) by applying symmetric bipolar square-wave voltages of different frequencies to the sample and measuring the changes in infrared transmittance, proportional to CDW strain. The frequency dependence of the electro-transmittance was fit to a modified harmonic oscillator response and the evolution of the parameters as functions of voltage, position, and temperature are discussed. We found that resonance frequencies decrease with distance from the current contacts, indicating that the resulting delays are intrinsic to the CDW with the strain effectively flowing from the contact. For a fixed position, the average relaxation time for most samples has a voltage dependence given by $\tau_0 \sim V^{-p}$, with $1 < p < 2$. The temperature dependence of the fitting parameters shows that the dynamics are governed by both the force on the CDW and the CDW current: for a given force and position, both the relaxation and delay times are inversely proportional to the CDW current as temperature is varied. The long delay times ($\sim 100\ \mu s$) for large CDW currents suggest that the strain response involves the motion of macroscopic objects, presumably CDW phase dislocation lines.

We have done frequency domain simulations to study charge-density-wave (CDW) polarization dynamics when symmetric bipolar square current pulses of different frequencies and amplitudes are applied to the sample, using parameters appropriate for NbSe$_3$ at $T = 90$ K. The frequency dependence of the strain at one fixed position was fit to the same modified harmonic oscillator response and the behavior of the parameters as functions of current and position are discussed. Delay times increase nonlinearly with distance from the current contacts again, indicating that these are intrinsic to the CDW with the strain effectively flowing from the contact. For a fixed position and high currents the relaxation time increases with decreasing current, but for low currents its behavior is strongly dependent on the distance between the current contact and the sample ends. This fact clearly shows the effect of the phase-slip process needed in the current conversion process at the contacts. The relaxation and delay times computed ($\sim 1\ \mu s$) are much shorter than observed in blue bronze ($> 100\ \mu s$), as expected because NbSe$_3$ is metallic whereas K$_{0.3}$MoO$_3$ is semiconducting. While our simulated results bear a qualitative resemblance with those obtained in blue bronze, we can not make a quantitative comparison with the K$_{0.3}$MoO$_3$ results since the CDW in our simulations is current driven, whereas the electro-optic experiment was voltage driven.

Different theoretical models predict that for voltages near the threshold $V_{on}$, quantities such as the dynamic phase velocity correlation length and CDW velocity vary as $\xi \sim |V/V_{on} - 1|^{-\nu}$ and $v \sim |V/V_{on} - 1|^\zeta$ with $\nu \sim 1/2$ and $\zeta = 5/6$. Additionally, a weakly divergent behavior for the diffusion constant $D \sim |V/V_{on} - 1|^{-2\nu + \zeta}$ is expected. Motivated
by these premises and the fact that no convincing experimental evidence is known, we carried out measurements of the parameters that govern the CDW repolarization dynamic for voltages near threshold. We found that for most temperatures considered the relaxation time still increases for voltages as small as $1.06V_{on}$ indicating that the CDW is still in the plastic and presumably in the noncritical limit. However, at one temperature we found that the relaxation time saturates with no indication of critical behavior, giving a new upper limit to the critical regime, of $|V/V_{on} - 1| < 0.06$.

KEYWORDS: Charge Density Wave, Blue Bronze, CDW Dynamics, CDW Polarization, CDW relaxation time.
CHARGE DENSITY WAVE POLARIZATION DYNAMICS

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DISserTATION

luis alejandro ladino gaspar

the graduate school
university of kentucky

2008
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DISSESSATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of Kentucky

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Dedicated to my parents, wife, mother-in-law and children.
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where $\Delta$ is the temperature dependent half Peierls gap, $v_F$ is the Fermi velocity and $m_e/m^*$ is the CDW reduced mass [19]. In this relation, effects of screening of the long Coulomb force are involved.
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1.1 Introduction

In 1955, Peierls showed that any electron-phonon interaction in a one dimensional metal at low temperatures will give rise to a state characterized by a periodic lattice distortion and a periodic modulation of the electronic charge density having twice the Fermi wave vector [21]. This was shown independently by Fröhlich in 1954 who also described how these distortions could transport charge [22]. Today, this distortion is referred to as a Charge Density Wave (CDW) and the charge transport associated with the motion of the distortion is referred to as Fröhlich or CDW conduction. The one dimensional nature of the chains induces the instability described by Peierls and Fröhlich, while the weak coupling of the chains allows for a finite transition temperature.

Beginning in the mid-1970s, examples of CDWs were found in a variety of materials. Typical examples of CDW transport are seen in inorganic linear chain compounds such as NbSe$_3$ (niobium triselenide) [23], TaS$_3$ (tantalum trisulfide) [24] and K$_{0.3}$MoO$_3$ (potassium molybdenum oxide, also known as blue bronze because of its deep blue color) [25].

The equilibrium CDW is pinned by a potential established by random defects and impurities and a moderate electric field is needed for depinning and CDW motion [26]. This threshold field is seen today as one of the signatures of CDW conduction.

Most of the unusual electronic properties are related to motion of the CDW in an applied field greater than the threshold field needed to depin it. In the CDW state, these anisotropic materials exhibit nonlinear conductivity, gigantic dielectric constants, unusual elastic properties and rich dynamical behavior [27]. Sliding charge density waves also have been used as prototype systems for study of the effects of quenched disorder on an elastic medium [1,28]. Thus, CDW materials have been the subjects of extensive theoretical and experimental studies.

The electro-optic effect of K$_{0.3}$MoO$_3$, which undergoes a phase transition into a semiconducting CDW state at $T_P = 180$ K [10], was discovered in 1994 by Brill and Itkis. They reported that the infrared transmission ($\theta$) changed in an applied electric field [29]. The changes in transmission ($\Delta \theta$) appeared to be thermally activated and vary with position in the sample: the transmission increases on the positive side of the sample and decreases on the negative. This electro-optic effect occurs for voltages $V > V_P$, the voltage at which one first observes CDW polarization, and they suggested that the electro-optic effect is caused by the polarization of the CDW state in the applied electric field. The changes in transmission signal are mostly associated with changes in the intraband absorption of thermally activated quasiparticles, whose density ($n_{qp}$) changes to screen deformations of the CDW in the applied field: $\frac{\Delta \theta}{\theta} \sim n_{qp} \sim \frac{\partial \phi}{\partial x}$, where $\phi$ is the CDW phase. The CDW materials exhibit a unique electro-optic effect which varies spatially throughout sample, occurs at extremely
small electric field ($\sim 100$ mV/cm), and occurs over a very wide (infrared) spectral range.

This thesis consists of six chapters. In chapter one, we review properties of sliding CDWs and present two different approaches related to the problem of current conversion between single particle and collective current at current contacts. Furthermore, we introduce a phenomenological model that describes the dynamics of CDW phase when an external force is applied. In chapter two, we describe the experimental procedure used to make our measurements. In chapter 3, we discuss our experimental results on the parameters that govern the CDW repolarization dynamics in blue bronze. This is achieved by measuring the changes in transmission and reflection along the sample when a symmetric bipolar square-wave voltage of different frequency and amplitude is applied to the sample. The behavior of the parameters as a function of the temperature are also analyzed and discussed. In chapter 4, I solve numerically a classical model to study CDW polarization dynamics in the quasi-one-dimensional conductor NbSe$_3$ at $T = 90$ K when symmetric bipolar square current pulses of different frequencies and amplitudes are applied to the sample. The results obtained bear a good qualitative resemblance with those obtained experimentally in blue bronze using our electro-optic technique. A fully detailed analysis is presented and comparison with the K$_{0.3}$MoO$_3$ response is made. In chapter 5 we describe the same system studied in chapter 3 but the main objective here was to experimentally determine the CDW phase relaxation time for voltages near the threshold at a fixed temperature. For voltages fairly near the threshold a critical behavior of some of the parameters is expected to be found. In chapter 6, I summarize my main conclusions.

1.2 Brief theory of Charge Density Waves

1.2.1 Peierls transition and CDW condensate

In order to describe the transition to a CDW ground state we will consider a one-dimensional free electron gas coupled to the underlying chain of ions through electron-phononon coupling. The corresponding Hamiltonian (expressed in second quantized form), usually referred to as the Fröhlich Hamiltonian, is given by [1]

$$H = \sum_{k} \epsilon_{k} a_{k}^{+} a_{k} + \sum_{q} \hbar \omega_{q} b_{q}^{+} b_{q} + \sum_{k,q} g_{q} a_{k+q}^{+} a_{k} (b_{-q}^{+} + b_{q})$$

(1.1)

The first term describes the electron gas where $a_{k}^{+}$ and $a_{k}$ are the creation and annihilation operators for the electron states with band energy $\epsilon_{k}$. In this approach, spin dependent interactions are not important, therefore spin degrees of freedom are not written and the density of states $n(\epsilon_{F})$ refers to one spin direction. The second term describes the lattice vibrations and $b_{q}^{+}$ and $b_{q}$ are the creation and annihilation operators for the phonon characterized by the wave vector $q$. The $\omega_{q}$ term represent the normal mode frequencies of the
ionic masses. The third term of the Hamiltonian accounts for the electron phonon interaction. The electron phonon coupling constant is 
\[ g_q = i \left( \frac{\hbar}{2M\omega_q} \right)^2 |q| V_q, \]
where \( V_q = V_{k-k'} \) is the Fourier transform of the potential of a single atom \( V(r) \) and \( M \) represent the ionic mass. In the case of a 1D electron gas, the coupled electron phonon system is unstable, and this instability has fundamental consequences for both the lattice and the electron gas [26].

The effect of the electron phonon interaction on the lattice vibrations can be described by establishing the equation of motion of the normal coordinates \( Q_q \). For small amplitude displacements:

\[ \dot{Q}_q = - \left[ \omega_q^2 - \frac{2g^2\omega_q}{\hbar} \chi(q, T) \right] Q_q \]  

(1.2)

The above equation of motion gives the renormalized phonon frequency

\[ \omega_{ren,q}^2 = \omega_q^2 - \frac{2g^2\omega_q}{\hbar} \chi(q, T) \]  

(1.3)

The term \( \chi(q, T) \) represents the generalized susceptibility\(^1\). For a one-dimensional free electron gas, \( \chi(q, T) \) has a maximum at \( q = 2k_F \) and becomes huge as the temperature decreases as shown in Fig. (1.1b). Consequently, the reduction or softening of the phonon frequencies will be most significant at these wave vectors. The softening of the \( 2k_F \) phonon, is called the Kohn anomaly [30]. The phonon dispersion relation as determined by Eq. (1.3) is shown in Fig. (1.1a) at various temperatures above the mean field transition temperature. With decreasing temperature, the renormalized phonon frequency goes to zero and this defines a transition temperature

\[ k_B T_{CDW}^{MF} = 1.14 \epsilon_0 e^{-\frac{1}{\lambda}} \]  

(1.4)

where \( \lambda \) is the dimensionless electron-phonon coupling constant: \( \lambda = 2g^2n(\epsilon_F)/\hbar^2\omega_{2k_F} \).

As mentioned before, the phase transition is defined by the temperature where \( \omega_{2k_F} \to 0 \) and is due to the strongly divergent response function of the 1D electron gas. Below the phase transition the renormalized phonon frequency is zero, indicating a "frozen-in" lattice distortion and causing a modulated lattice displacement and a modulated electronic density given by [1]

\[ \langle u(x) \rangle = \Delta u \cos(2k_Fx + \phi) \]  

(1.5)

\[ \rho(x) = \rho_0 + \rho_1 \cos(2k_Fx + \phi) \]  

(1.6)

\(^1\)When an electron gas system is subject to a time independent periodic potential (perturbation) \( \phi(\vec{r}) \) it causes an induced charge \( \rho^{ind}(\vec{r}) \). These two quantities are related as \( \rho^{ind}(\vec{r}) = \chi(\vec{q})\phi(\vec{r}) \), where \( \chi(\vec{q}) \) is the so-called Lindhard response function or generalized susceptibility. See Ref. [30]
where \( \Delta u = \sum_q \left( \frac{\hbar}{2NM\omega_0} \right) \frac{1}{2} |\Delta| \), \( \rho_0 \) is the uniform electronic density in the metallic state and \( \rho_1 = \frac{\rho_0 \Delta}{\hbar v_F k_F \lambda} \) is the amplitude of the charge density modulation. The dispersion relation, the electronic density, and the equilibrium lattice positions are shown, at \( T = 0 \) in Fig.(1.2) in the special case of a half filled band, in which case the lattice distortion is a dimerization. The ground state exhibits a periodic modulation of the charge density and a lattice distortion and the single particle excitations have a gap \( \Delta \) at the Fermi level. This turns the material into an insulator upon the formation the the CDW ground state.

The CDW can be either commensurate or incommensurate with respect to the underlying lattice. If the CDW period \( \lambda = \frac{\pi}{k_F} \) is a rational fraction of the lattice constant \( a \), the CDW is commensurate and it has a preferred position. In many cases, the period \( \lambda \) is incommensurate with the underlying lattice (i.e., is not a rational fraction of the lattice constant \( a \)), and the phase can assume an arbitrary value for a perfect crystal. Therefore, an incommensurate CDW state does not have a preferred ground state and the ground state energy of the system would not change if the CDW is displaced. Because of this, Fröhlich [22] suggested that the ability of an incommensurate CDW to move freely in a crystal may be a possible mechanism of superconductivity. Instead, the CDW is usually pinned to the lattice by impurities, defects, or by its commensurability with the lattice, locking it into a preferred ground state [22,26]. Consequently, contrary to Fröhlich’s expectation, the collective mode contribution to the dc conductivity at low electric fields is zero.
Figure 1.2: Electronic density, equilibrium lattice positions and dispersion relation in a one dimensional metal at $T = 0$. a) In the absence of electron-electron or electron-phonon interaction: the electron states are filled up to the Fermi level $\epsilon_F$. b) In the presence of an electron-phonon interaction the distortion with period $\lambda = \frac{\pi}{k_F}$ opens up a gap at the Fermi level. (Peierls distortion). The case shown corresponds to a half-filled band and a dimerization. Plots taken from Ref. [1].

However, if an electric field is applied that is strong enough to overcome the pinning potential of impurities, the CDW can be depinned and can slide in the crystal. The sliding of the CDW results in an increase of the conductivity of the crystal. This non-Ohmic behavior is a unique character of CDW (and related spin density wave) materials. The conductivity saturates at the value of its normal state due to scattering of the CDW from the normal electrons.

1.2.2 Similarities and differences between Superconductors and CDW conductors

In superconductors and CDW conductors there is an additional degree of freedom characterized by the complex order parameter $\Delta = |\Delta|e^{i\phi} [1]$, where $|\Delta|$ is defined as the single particle gap, see Fig.(1.2). In superconductors this is the well-known superconducting gap, while in CDWs this is the Peierls gap. The appearance of a gap leads to a finite amplitude coherence length $[5, 3]$ defined as $\xi_0 \approx \hbar v_F/|\Delta|$, with $\hbar$ Planck’s constant and $v_F$ the Fermi velocity. Using this definition $\xi_0 \approx 1$ nm, for CDW materials, the same order as the CDW wavelength $\lambda_{CDW}$.

a) In superconductors, the phase of order parameter $\phi$ has the meaning of the quantum mechanical phase while the CDW phase characterizes the position of the CDW respect to the underlying lattice. This distinction shows up as the Meissner effect and nondissipative current flows in superconductors, and the absence of similar effects in CDW conductors [31].
b) In superconductors, the partial derivative of the phase with respect to time represents the voltage, \( \frac{\partial \phi(x,t)}{\partial t} \sim V \). In CDW materials, the partial derivative of the phase respect to time represent the CDW current, \( \frac{\partial \phi(x,t)}{\partial t} \sim i_c \).

c) The interaction of the condensate with impurities in these cases is different: the ordinary (nonmagnetic) impurities in superconductors do not affect the order parameter \( \Delta \) and do not break the translational invariance of the system, while such impurities in CDW conductors suppress \( \Delta \) and break the translational invariance; they cause, in particular, pinning of the CDW [31].

d) In spite of the differences between superconductors and CDW conductors, their kinetic properties can both be described using the Ginzburg-Landau formalism [31].

1.3 CDW pinning

In quasi-one dimensional CDW materials the interaction between CDW and impurities results in some of the most remarkable transport effects ever discovered [1]. The translational invariance of an incommensurate CDW is destroyed in the presence of impurities (or other crystal defects), so the CDW tends to be pinned. For an applied electric field greater than the threshold field \( E_T \), the CDW can depin from the impurities and slide through the crystal, resulting in non linear dc conduction [32,33]. Coherent current oscillations [narrow band noise, NBN] [33] observed in response to dc fields and mode locking phenomena (including Shapiro steps) observed in response to combined of ac and dc fields [34] establish that the pinning is periodic in CDW displacements of integral numbers of wave lengths. Thus, pinning mechanisms plays a crucial influence on the static and dynamic properties of charge density waves.

The problem of pinning due to many impurities distributed randomly in the crystal has been treated within the framework of the Ginzburg-Landau formalism (Fukuyama and Lee [35], Lee and Rice [36]). The time-independent FLR hamiltonian in \( d \) dimensions is given by

\[
H = \frac{1}{2} \int d^d\vec{r} \tilde{K}(\nabla^2 \phi)^2 + \sum_{i=1}^{N_{\text{imp}}} v \rho_1 \cos[Q \cdot \vec{r}_i - \phi(\vec{r}_i)] + \frac{1}{2} \int d^d\vec{r} \frac{\tilde{p}_{e\text{ff}}}{Q^2} \vec{E} \cdot \vec{Q} \tag{1.7}
\]

The first term describe the CDW elastic energy, the second term describe the interaction of the CDW with pinning sites located at \( \vec{r}_i \), where \( v \) is the impurity potential, \( \rho_1 \) is the amplitude of the CDW modulations: \( \rho(\vec{r},t) = \rho_c + \rho_1 \cos[Q \cdot \vec{r} + \phi(\vec{r},t)] \); and the third term describes the coupling of the CDW phase with the electric field \( \vec{E} \), where \( \tilde{p}_{e\text{ff}} \) is an effective condense charge density. The transverse dimensions have been rescaled in terms of the strain coefficients anisotropies as \( \tilde{x} = \xi_{s\text{x}}/\xi_{s\text{z}} \) and \( \tilde{y} = \xi_{s\text{y}}/\xi_{s\text{z}} \); \( \tilde{K} = \xi_{s\text{z}}K/\xi_{s\text{z}}^2 \) is the rescaled CDW elastic coefficient; \( \tilde{p}_{e\text{ff}} = \xi_{s\text{y}}\tilde{p}/\xi_{s\text{z}}^2 \) is the rescaled effective charge density coupling the CWD to the electric field; and the electric field is applied along the quasi-one
dimensional direction $z$. In $T=0$ mean field theory, $K = \hbar v_F / 2\pi A_0$ where $v_F$ is the Fermi velocity along $z$ and $A_0$ is the unit cell cross-sectional area normal to $z$.

In the FLR model, the CDW is an elastic medium that can adjust its phase $\phi(x,t)$ (Eq.(1.6)) in the vicinity of impurities and defects. FLR showed that the nature of the pinned state is determined by balancing the impurity energy gain associated with optimizing the CDW phase at each impurity size and the elastic energy cost required for phase deformation between impurities. CDW motion is possible when the applied electric field is large enough to overcome a threshold value, which results from the balance of elastic and impurity pinning energy.

Defining $\epsilon_i = E_I/E_E$, where $E_I = v\rho_1$ is the characteristic energy per impurity and $E_E = \tilde{K}\tilde{n}_i^{-1+2/d}$ is the characteristic CDW elastic energy, with $\tilde{n}_i$ as the impurity concentration; the FLR model distinguishes two regimes: strong and weak pinning.

1. In the strong pinning regime, ($\epsilon_i > 1$), the impurity pinning force is larger than the elastic force in the CDW. The CDW phase is fully adjusted at each impurity and amplitude collapse is needed for local phase motion [37].

2. In the weak pinning regime, ($\epsilon_i < 1$), the elastic forces are larger than the impurity pinning force. The CDW phase is adjusted to many randomly distributed impurity sites and the CDW is collectively pinned by elastic deformations of its phase on length $\ell_\phi$. See Fig.(1.3).

Thus, impurities which couple directly to the phase $\phi$ of the condensate, destroy the long-range order and lead to a finite phase-phase correlation length (also known as the FLR length or phase-coherent length) $\ell_\phi$ and is defined from $\langle \phi(\vec{r}), \phi(0) \rangle \approx \exp(-r/\ell_\phi)$. The values of the phase-phase coherent length $\ell_\phi$, the threshold field $E_T$ and the energy per phase coherent domain are shown in Table 1.1.

Within the framework of the FLR model, for the weak pinning, the values the phase coherence length, the pinning-energy gain of a phase coherent volume and threshold electric
field depend on dimensionality of the CDW as shown in the Table 1.1. A comparison of the same quantities, for the strong and weak pinning cases in 3 dimensions is shown in Table 1.2, [2].

Table 1.1: For weak pinning: phase-phase coherent length $\ell_\phi$, threshold field $E_T$ and pinning energy per phase-coherent domain $U_{dom}$. Taken from Ref. [2].

<table>
<thead>
<tr>
<th>$d$</th>
<th>$\ell_\phi$</th>
<th>$E_T$</th>
<th>$U_{dom}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$\frac{45K^2}{(v_{p1})^2n_i}$</td>
<td>$\frac{Q(v_{p1})^2n_i^2}{1000\rho_{sff}K^3}$</td>
<td>$\frac{300K^3}{(v_{p1})^2n_i}$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{6.5K}{(v_{p1})^{3/2}n_i}$</td>
<td>$\frac{Q(v_{p1})^2n_i}{20\rho_{sff}K}$</td>
<td>$6.5\tilde{K}$</td>
</tr>
<tr>
<td>1</td>
<td>$\frac{3.5K^{2/3}}{(v_{p1})^{2/3}n_i}$</td>
<td>$\frac{Q(v_{p1})^{1/3}n_i^{2/3}}{6\rho_{sff}K^{1/3}}$</td>
<td>$2(v_{p1})^{2/3} K^{1/3} \sqrt[3]{n_i}$</td>
</tr>
</tbody>
</table>

Table 1.2: Comparison: Strong vs weak pinning: phase-phase coherent length $\ell_\phi$, threshold field $E_T$ and pinning energy per phase-coherent domain $U_{dom}$. Taken from Ref. [2].

<table>
<thead>
<tr>
<th></th>
<th>$\ell_\phi$</th>
<th>$E_T$</th>
<th>$U_{dom}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>$\frac{45K^2}{(v_{p1})^2n_i}$</td>
<td>$\frac{Q(v_{p1})^2n_i^2}{1000\rho_{sff}K^3}$</td>
<td>$\frac{90K^3}{(v_{p1})^2n_i}$</td>
</tr>
<tr>
<td>Strong</td>
<td>$\frac{\frac{1}{3}^{-1/3}n_i}{\rho_{sff}}$</td>
<td>$\frac{Q(v_{p1})n_i}{\rho_{sff}}$</td>
<td>$v_{p1}$</td>
</tr>
</tbody>
</table>

The 2D and 1D weak pinning expressions must be modified when dimensionality is imposed by a length scale cutoff, i.e., $\ell_\phi^{3D} > \tilde{t}$ for 2D confinement, or when $\ell_\phi^{1D} > \tilde{t}$ and $\tilde{w}$ for 1D confinement, where $\tilde{t}$ and $\tilde{w}$ represent the thickness and width of the sample. The new values of phase-phase coherent length $\ell_\phi$, threshold field $E_T$ and pinning energy per phase-coherent domain $U_{dom}$ are shown in Table 1.3, [2].

Table 1.3: Weak pinning predictions in $d = 2$ and $d = 1$ where dimensionality is imposed by confinement: Phase-phase coherent length $\ell_\phi$, threshold field $E_T$ and pinning energy per phase-coherent domain $U_{dom}$. Taken from Ref. [2].

<table>
<thead>
<tr>
<th></th>
<th>$\ell_\phi$</th>
<th>$E_T$</th>
<th>$U_{dom}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d = 2$</td>
<td>$\frac{10\tilde{K}^{1/2}(v_{p1})^{1/3}n_i}{\rho_{sff}K\tilde{t}}$</td>
<td>$\frac{Q(v_{p1})^{2/3}n_i}{30\rho_{sff}K\tilde{t}}$</td>
<td>$10\tilde{K}\tilde{t}$</td>
</tr>
<tr>
<td>$d = 1$</td>
<td>$\frac{7.5K^{2/3}(\tilde{w}^{1/3}n_i^{2/3}}{(v_{p1})^{2/3}n_i}$</td>
<td>$\frac{Q(v_{p1})^{1/3}n_i^{2/3}}{9\rho_{sff}K^{1/3}n_i} \tilde{w}^{2/3}$</td>
<td>$3(v_{p1})^{2/3} K^{1/3} \sqrt[3]{n_i} \tilde{w}^{2/3}$</td>
</tr>
</tbody>
</table>

The use of nanolithographic techniques has allowed experimentalist to reduce the size of
CDW materials and therefore opened the way to study finite-size effects in CDW materials. Thus McCartney et al. [2] showed a crossover from 3-dimensional ($d = 3$) to 2-dimensional ($d = 2$) collective pinning in NbSe$_3$ when the crystal thickness $\tilde{t}$ was smaller than the phase-coherent length $\ell_\phi$. In this case the threshold field dependence on the sample thickness switched from being independent to $E_T \propto \frac{1}{t}$. Recently, Slot et al. [16] using NbSe$_3$ structures with thickness $\tilde{t}$ less than the phase-phase coherent $\ell_\phi$ could probe the width-dependent pinning and the $d = 2$ to $d = 1$ crossover by measuring the cross-sectional area dependence of the threshold field, i.e., $E_T \propto \frac{1}{t}$ for $d = 2$ and $E_T \propto \frac{1}{t^{3/d}}$ for $d = 1$ as predicted in Table 1.2.

The dependence of the threshold field on the impurities concentration has also been confirmed experimentally. For the weak pinning case and $d = 3$, Brill et al. [38] studied more than 22 samples of NbSe$_3$ doped with Ta impurities and found that the characteristic field $E_0$ and the threshold field $E_T$ obey a $\tilde{n}^2$ behavior ($\tilde{n}$ varied from 100 to 1900 ppm) as predicted, see Table 1.2.

The temperature dependence of the threshold electric field is shown in Fig.(1.4) for NbSe$_3$ [2] and K$_{0.3}$MoO$_3$ [3]. Notice again that in the case of NbSe$_3$ the finite-size effect of the crystal makes the threshold electric field $E_T$ increase as the thickness of the sample decreases for a fixed temperature. The temperature behavior of $E_T$ for K$_{0.3}$MoO$_3$ is different from that of NbSe$_3$ as can be observed from the pictures, and is not understood.

Values of correlation length measured along the highly conduction direction and perpendicular to it for heavily Ta doped and undoped NbSe$_3$ using high resolution x-ray scat-
tering [20] are shown in Table 1.4. Measurements of the longitudinal and transversal correlations length in Rb and W-doped K$_{0.3}$MoO$_3$ has revealed comparable magnitudes [39].

Table 1.4: Correlation length of NbSe$_3$ and heavily Ta-doped NbSe$_3$: $b^*$ and $a^*$ indicate direction of high conductivity and perpendicular to it respectively. Taken from Ref. [20].

<table>
<thead>
<tr>
<th>Direction</th>
<th>NbSe$_3$</th>
<th>Heavy Doped NbSe$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b^*$</td>
<td>$\ell_{b^*} = 0.9 \mu$m</td>
<td>$\ell_{b^*} = 2.5\mu$m</td>
</tr>
<tr>
<td>$a^*$</td>
<td>$\ell_{a^*} = 0.1 \mu$m</td>
<td>$\ell_{a^*} = 1.9\mu$m</td>
</tr>
</tbody>
</table>

1.4 CDW Deformation, Strain, Phase-Slip and Screening

Charge density waves are subject to deformations when electric fields are applied to them. As shown in Fig.(1.5), for an applied electric field $E_P < E \leq E_T$, where $E_P$ and $E_T$ are called the lower and higher threshold fields respectively, the CDW deforms locally (i.e., strained), overcomes the pinning in the bulk of the sample but remains pinned at the contacts. However, for $E > E_T$ the CDW depins at the contacts and slides carrying current into the contacts, but beyond the contacts where $E \approx 0$ the CDW remains pinned. Consequently, CDW motion results in compression of the CDW near one contact and expansion or rarefaction near the other.

Electrical contacts play a crucial role in determining the structure of the sliding CDW. CDW current flow requires a mechanism for adding and removing CDW wave fronts at the contacts and for converting between collective current and single particle current. This mechanism is provided by phase-slip [36, 40–42], and is driven by gradients in the CDW phase $\phi(x, t)$.

While the precise mechanisms by which phase slip occurs in CDW materials is unclear, it likely involves (1) formation of dislocation lines, loops or other CDW defects, and (2) motion/growth of the defects out of the crystal so as to remove CDW wavefronts in the crystal cross section. For samples of finite cross section, phase slip presumably develops as dislocation loops (DLs) [43, 44], which climb to the crystal surface, each DL allowing the CDW to progress by one wavelength [40].

The electric field induced deformations in CDW involve phase gradients $\partial \phi / \partial x$ and a variation of the CDW wave vector by $\Delta Q$ with respect to its non deformed wave vector $Q = 2k_F$. These deformations have been studied by several groups using different indirect methods, such as Itkis and Brill through the electro-optic effect [45] by making measurements of the electromodulated infrared transmission in K$_{0.3}$MoO$_3$ and by the Cornell group via electronic transport measurements on NbSe$_3$ using multiple contact samples [9, 46]. The length of samples used in both techniques is $\approx 1$ mm. The emerging results from these two
dissimilar techniques suggests a linear relation between $\Delta Q$ and position $x$ (measured from the midpoint between the contacts) in the central part of the sample. However, for points near the current contacts ($\approx 100 \mu m$) this relation deviates from being linear as the driving force becomes larger.

On the other hand, x-ray measurements yield direct information on the spatial distribution of the CDW deformations. DiCarlo et al. [5] reported the results of deformations on NbSe$_3$ using a 0.8 mm wide x-ray beam on a 4.5 mm long sample at $T = 90$ K. The data from this experiment also suggested an approximately linear variation of $\Delta Q$ with $x$ in the central part of the sample, but experimental limitations did not allow the contact regions to be explored. These results supported the idea that the magnitude of the compressions and expansions measured as $\Delta Q$ vary according to

$$\Delta Q(x) = \frac{\partial \phi}{\partial x} = \varepsilon(x)Q = \frac{en_1}{QK}V_{ps}xL$$

(1.8)

where $V_{ps}$ is the phase-slip voltage, which is the applied voltage in excess of that required to overcome pinning and damping forces; $K$ is the CDW elastic constant, $en_1$ is the CDW charge density and $L$ is the contact separation and $x$ is the position measured from the midpoint between the contacts. The variation of the CDW phase with position causes a strain defined as $\varepsilon = Q^{-1}\partial \phi/\partial x$. Under this model, pioneered by Ramakrishna [41, 42, 47], the phase slip occurs by homogeneous thermal nucleation of dislocation loops and

Figure 1.5: A CDW crystal with two current contacts. a) For $E_P < E \leq E_T$ the CDW remains pinned. b) For $E > E_T$ the CWD depins at the contacts and conveys current. But the CDW well beyond the current contacts remains pinned, so that the CWD becomes compressed near one contact and stretched near the other.
inhomogeneous (i.e., defect-assisted) process [36, 41, 48].

The relation between the CDW current $i_c$ and the phase-slip voltage $V_{ps}$ was experimentally determined by several groups [4, 49, 50] on NbSe$_3$ using electric transport methods introduced by Gill [48],

$$i_c = I_0 \left( \frac{V_{ps}}{V_a} \right) \exp \left( \frac{-V_a}{V_{ps}} \right)$$

where $I_0 \propto L$ and $V_a$ increases strongly with decreasing temperature.

As mentioned earlier, the addition and removal of phase fronts at the current contacts occur via phase slip, and it is triggered by nucleation of dislocation loops in the CDW superlattice according to Ramakrishna et al. [42]. Within the framework of this model, the energy of a critical dislocation loop varies inversely with CDW strain, $\varepsilon$; and the $V_{ps}$ required to obtain a given nucleation /phase slip rate decreases with increasing temperature (see Fig. (1.6b)), suggesting that phase slip is thermally activated. The current and temperature dependence of $\Delta Q$ and $V_{ps}$ on NbSe$_3$ using x-ray measurements is shown in Fig. (1.6). For the sake of completeness and comparison, the curves obtained by electric transport measurements [4] are also shown.

The local nucleation rate or phase slip rate $r_{ps}$ is given by

$$r_{ps} = -\text{sgn}(\varepsilon(x))r_0 \cdot \exp \left[ -\frac{en_1}{Q} \frac{V_a}{2KQ|\varepsilon(x)|} \right] = -\text{sgn}(\varepsilon(x))r_0 \cdot \exp \left[ -\frac{\varepsilon_B}{|\varepsilon(x)|} \right]$$

(1.10)

where $\text{sgn}(x)$ is the signum function and $\varepsilon_B = \frac{en_1V_a}{2KQ^2}$. $V_a$ and $r_0$ are related to the barrier height and attempt rate for dislocation loop nucleation, respectively [41, 42, 47]. The nucleation rate is strongly dependent on the strain $\varepsilon(x)$, thus the phase slip is large at the contacts where the strain is largest. The local phase-slip rate $r_{ps}$ in terms of the CDW current density $j_c$ is given in the Ramakrishna model [42] by

Figure 1.6: Variation of the wave vector $\Delta Q$ and phase slip voltage $V_{ps}$ as a function of: a) current at $T = 90K$ in NbSe$_3$ and b) temperature for a fixed current in NbSe$_3$. Solid curves are the predicted curves using electric transport measurements [4] and the points were determined by DiCarlo et al. [5] using x-ray measurements.
Figure 1.7: CDW current density \( j_c(x) \) vs temperature measured by Lemay et al. [6] using multiple contact technique. The driving current density \( j_{\text{total}} \) was varied such that \( j_c = 8.3 \, \mu\text{A/m}^2 \) at the center of the sample for all temperatures. This CDW current density corresponds to a driving current \( j_{\text{total}} = 4.3 \times j_T \) at \( T = 90 \, \text{K} \). For clarity, curves are shown normalized to their maximum value and successive curves are shifted down by 0.2. The connecting lines for \( T = 105 \, \text{K} \) and \( T = 120 \, \text{K} \) are guides to the eye. The dotted vertical lines indicate the positions of the current contacts at \( x \pm L/2 = 355 \, \mu\text{m} \). Taken from Ref. [6].

\[
r_{ps}(x) = -\frac{Q}{en_c} \frac{\partial j_c}{\partial x}
\]  
(1.11)

Using electronic transport measurements, Lemay et al. [6] could determine the spatial distribution of the CDW current density \( j_c(x) \) in NbSe\(_3\) at different temperatures and directions of the CDW current as shown in Fig.(1.7). One important feature to highlight here is that the size of the region near each current contact where appreciable phase-slip occurs is less than 40 \( \mu\text{m} \) for \( T \) near 120 K but grows to \( \sim 100 \, \mu\text{m} \) at lower temperatures. From these measurements Lemay et al. [6] also could verify the relation between phase-slip rate \( r_{ps}(x) \) and the strain \( \varepsilon(x) \) given by the Eq.(1.10). However, the relation is not unique but varies with the distance from the current contacts as shown in Fig.(1.8).

Five years after DiCarlo et al. [5] reported results on NbSe\(_3\) using x-ray measurements, Brazovskii et al. [51], using the same technique but with a higher resolution, reported results on the deformations of the CDW wave vector in a 4.1 mm long sample at \( T = 90 \, \text{K} \), when the CDW is in the sliding state. They observed a steep variation of \( Q \) in the vicinity of the contacts by applying direct currents. Figure(1.9) shows the "double shift" \( q \pm = \Delta Q(+1) - \Delta Q(-1) \) as function of the beam position \( x \) along the left-hand of the sample \( 0 < x < 2 \, \text{mm} \) for applied pulsed and dc currents of \( |I| = 4.6 \, \text{mA} = 2.13I_T \). For
Figure 1.8: Phase-slip rate $r_{ps}(x)$ vs CDW strain $\varepsilon(x)$ at four positions $x$ from the current contact at $T = 90$ K. Each data point correspond to a different driving current. According to the bulk nucleation model, Eq.(1.10), the data for the various positions should collapse onto a unique straight line. Instead, $r_{ps}$ for a given $\varepsilon$ increases with distance from the current contact. The dotted line is a fit of the $x = 0$ data to Eq.(1.10). Taken from Ref. [6].

both types of current, $q^\pm$ shows a linear variation with position $x$ in the central part of the sample ($0.7 < x < 2.0$), and no difference is observed between direct and pulsed currents. However, in the range $0 < x < 0.7$ mm, there is exist a noticeable difference in $q^\pm$ for the two types of currents. These differences suggest a spatially dependent, relaxational behavior for the CDW deformations, the fastest relaxation occurring at the contact position. This relaxational behavior has been observed and studied in our laboratory using an electro-optical technique [45].

The result of these measurements confirm that the CDW is deformed in the current carrying state with different effects near contacts and in the bulk, and are strongly contradictory to Ramakrishna’s results. In particular, the relation given by Eq.(1.8) loses validity, as had been already evidenced by indirect methods [9, 45].

In his model, Brazovskii consider a quantity $\eta$ defined as

$$\eta = \mu - U \sim q = \Delta Q \sim \varepsilon$$

(1.12)

where $\mu$ is the electrochemical potential of the normal carriers and $U$ is the potential energy of the condensate electrons. The CDW is deformed whenever the energy of the condensed electrons does not coincide with the electrochemical potential of the normal carriers. The exchange between normal carriers and the condensate results finally in the equilibration between $\mu$ and $U$ and is mediated via nucleation and growth of dislocation loops.
Figure 1.9: Double-shift \( q \pm (x) = \Delta Q(+I) - \Delta Q(-I) \) (in units of \( b^* \)) for direct (●) and pulsed (○) current (\( I/I_T = 2.13 \)). The full line shows the exponential fit from Eq.(1.14) near the contact (\( 0 < x < 0.5 \)) and a linear dependence for \( 0.7 < x < 2 \). The dash-dotted line extrapolates the exponential fit into the central section. The vertical dashed line represents the contact boundary; the horizontal dashed line, the line of zero shift. \( \text{NbSe}_3, T = 90 \text{ K}. \) Taken from Ref. [7]

Also in this model, the conversion rate \( R \) between normal carriers and condensed carriers can be decomposed into passive \( R_p \) and active \( R_a \) contributions as

\[
R(\eta, j_c) = R_p(\eta) + R_a(\eta, j_c)
\]

(1.13)

For the case of passive conversion (wherein the CDW motion plays no role) there are two extreme scenarios: the first refers to an ideal host crystal (both in the bulk and at the surface) where only spontaneous thermal homogeneous nucleation is present, so that

\[
R = R_0 \exp(-\eta_0/|\eta|), \quad \eta \sim \Delta Q.
\]

The other extreme is the heterogeneous case that refers to samples with sufficiently large density of imperfections acting as nucleation centers for supercritical dislocation loops; the simplest form for this case being \( R \sim \eta \).

The active case emerges for fast enough CDW motion when the dislocation loops are created by the CDW sliding through the bulk or surface defects. The easiest form taken by \( R \) is

\[
R = R(\eta, j_c) = \eta j_c.
\]

An active process in the bulk corresponds to the creation of pairs of dislocation loops [51] at strong impurities, thus providing for a local slowing down of the CDW motion. Another branch of this scenario, possibly the most realistic one for clean thin samples, relies upon the ultimate creation of dislocation lines at crystallographic steps on the surface.

Whatever might be the mechanism for the creation of dislocation lines or dislocation
loops, their subsequent propagation across the sample is affected by interaction of these lines with impurities. These lines are subjected to a collective or local pinning [52]. The collective pinning implies the existence of a critical value \( \eta_t \) below which the motion is hindered; the dislocation loops will not expand so that \( R = 0 \) if \( |\eta| < \eta_t \).

To simulate his experimental results, Brazovskii et al. [53] developed a model in terms of intensive nucleation process of dislocation loops at the host defects. He assumed that \( R = 0 \) at \( \eta < \eta_t \) and found that \( \Delta Q \) is given by

\[
q(x) = \Delta Q(\pm 1) = \frac{J_0 \lambda}{D_n g} \left[ \exp\left(-\frac{|x + a|}{\lambda}\right) - \exp\left(-\frac{|x - a|}{\lambda}\right) \right]
\]

where \( J_0, \lambda, D_n = \sigma_n \ell^2 \) and \( 2a \) are the current applied at the contacts, the characteristic length scale of the phase slip distribution, the normal carrier diffusion coefficient (with \( \ell \) the normal carrier screening length) and the sample length. Figure 1.10 shows the calculated double shift \( 2q(x) \) profile against the experimental data shown in fig.(1.9). Note that the linear variation in the center of the sample is a consequence of the cutoff of \( \eta_t \). However, Eq.(1.14) states that for long samples \( (a >> \lambda) \) there will be no linear gradient in the center as can be seen in Fig.(1.11). The carrier conversion will be complete, and the CDW deformation in the central region will be reduced to zero. Consequently, the large gradients at the sample center observed by the Cornell group using transport measurements [9] can be interpreted as due to an extreme size effect: the distance between contacts is so short that only a small part of the applied normal current is converted, so that the currents \( j_c \) and \( j_n \) stay far from their equilibrium values. In such a case, Eq.(1.14) is close to linear with only small increments at the current contacts.
Figure 1.11: Double shift $q_{\pm}$ as a function of position according to Eq.(1.14) for different sample lengths $L = 2a$. For simplicity we have taken $\frac{\pi \delta n}{D_{n,q}} = 1$ and $\lambda = 300 \mu$m. a) $L = 1$ mm b) $L = 2$ mm c) $L = 4$ mm and d) $L = 6$ mm.

Additionally, in the model of the Cornell group [9] the quasiparticle conductivity was treated as a constant, whereas in Brazovskii’s model [51] the uncondensed and thermally excited quasiparticles respond differently to CDW strains, resulting in local changes in their density, larger strains near the contacts, and more extended regions of current conversion. The strains observed in reference [7] near the center of the sample persisted even when the applied voltage was removed; [5, 51, 54] as emphasized in Reference [51], pinning of CDW phase dislocations is presumably responsible for these nonequilibrating strains.

### 1.4.1 Effects of Quasiparticle Screening

In the case of the nonuniform deformation of the CDW, space dependent variation of its charge density $\delta \rho(x) = e \delta n_{CDW}$ appears in the sample [26, 55], which is proportional to the gradient of the CDW phase $\partial \phi / \partial x$. These local variations of the charge density must be screened by free carriers [56–59].

$$\Delta n_{CDW} = \frac{1}{\pi \cdot A} \frac{\partial \phi}{\partial x} = -\Delta n_{qp} \tag{1.15}$$

where $A$ is the area/conducting chain.

As a result of the CDW deformations induced by electric fields or temperature, the chemical potential level $\mu$ will be shifted with respect to the middle of the energy gap (band bending). The corresponding variation of the Peierls gap is proportional to $(\partial \phi / \partial x)^2$ and for $\Delta Q \ll Q$ and $\mu \ll \Delta$ is negligible [60]. The relation between the variation of the CDW...
wave vector $\Delta Q$ and the chemical potential $\mu$ using conditions of electro-neutrality is given by [61, 62]

$$\frac{\Delta Q}{Q_0} = -2 \frac{1}{n_0} Ne^{-\Delta T} \sinh \left( \frac{\mu}{T} \right)$$

(1.16)

where $N$ is the effective density of states, which is assumed to be equal for electron and holes, $Q_0$ is the value of $Q$ at equilibrium and $n_0 = Q_0/\pi$. Generally speaking, any variation of $Q$ from thermodynamic equilibrium leads to variation of the properties of one dimensional conductors, determined by quasiparticles [58, 60, 62].

In CDW materials with fully gapped Fermi surface, such as $K_{0.3}MoO_3$ and $TaS_3$, a small deformation can lead to a considerable change in conductivity. This effect is sensitive to temperature, because the number of excited charge carriers decreases strongly with decreasing temperature. Thus, the largest changes in conductivity are found at low temperatures. The effect of deformations on the conductivity in $K_{0.3}MoO_3$ and $TaS_3$ is similar to the effect of doping on on the conductivity or ordinary semiconductors. In analogy with semiconductors, this effect of CDW deformations is sometimes called strain induced doping [63].

### 1.5 Electro-Optic effect

As was discussed in section 1.4, electric field induced deformations in CDW ($\sim \partial \phi / \partial x$) cause a variation of its charge density according to Eq.(1.15). This spatial variation of the charge is the cornerstone of the electro-optic effect [29].

In the electro-optic effect, the changes in infrared transmission along the CDW on $K_{0.3}MoO_3$ or $TaS_3$ depends on changes in the quasi particle density. Consequently, the single particle resistivities in these materials also vary with position between the current contacts and with the direction of the current flow.

On the other hand, the transmissivity of an absorbing medium of thickness $t$ is given by [64]

$$\theta \approx (1 - R)^2 \exp(-\alpha \cdot t)$$

(1.17)

where $R$ is the reflectivity, $\alpha$ is the absorption coefficient. This formula applies to the transmission of light through an optically thick medium ($\alpha \cdot t \gg 1$).

Taking a variation of $\theta$ respect to $R$ and $\alpha$, we get

$$\frac{\Delta \theta}{\theta} \approx -t \cdot \Delta \alpha - 2 \frac{\Delta R}{(1 - R)}$$

(1.18)

However the electromodulated reflectance signal is expected to have a relatively weak dependence on the quasiparticle density and it is mostly dominated by the phonon lines. For a review of the effects of CDW polarization on phonons on $K_{0.3}MoO_3$ see Refs. [65] and [66].
Therefore, neglecting changes in $R$, the electromodulated transmission signals due to the changes in the quasiparticle density can be written as
\[
\frac{\Delta \theta}{\theta} \approx -\Delta \alpha \approx \Delta n_{qp} \approx \frac{\partial \phi}{\partial x}
\] (1.19)

Hence, the relative changes in IR transmission can be used to probe the local gradient of the CDW phase $\phi$, in the applied electric field.

Whereas NbSe$_3$ remains metallic in the CDW state, in most other sliding CDW materials, all conduction band are completely gapped in the CDW state [26]. The CDW’s in semiconducting materials such as K$_{0.3}$MoO$_3$ and TaS$_3$ are much less coherent than in NbSe$_3$, preventing x-ray measurements of the spatial dependence of the strain. Analysis of position dependent transport properties of these materials has also been complicated by the difficulty in preparing ohmic but non-perturbative contacts [46]. The absence of uncondensed electrons [67] furthermore complicates the analysis of transport properties because as the density of thermally excited quasiparticles falls at low temperatures, soliton-like defects can dominate even the low-field, Ohmic, conductance [46]. Hence, measuring changes in infrared transmission and reflection allows one to determine position and time dependent changes in the semiconducting CDW phase in TaS$_3$ [67] and K$_{0.3}$MoO$_3$ [29,45,68], which has not been possible with other techniques.

### 1.5.1 Spatial and voltage dependence of the Electro-Optic effect.

Section 2.1 describes the technique used to measured the changes in transmission in a K$_{0.3}$MoO$_3$ crystal when a small portion of it is simultaneously radiated with IR light and a square wave voltage is applied. The electro-transmission of blue bronze does not appear until the applied field is strong enough to polarize the CDW state; the effect usually peaks at the dc threshold field and starts decreasing in magnitude with higher field as shown in Fig.(1.12a). The solid line shows the current as a function of voltage across the sample. Above threshold $V_T$, the CDW is sliding and the current becomes nonlinear with excess current $I_{CDW} = I - \frac{V}{R_0}$, where $I$ is total current, $V$ is the voltage across the sample and $R_0$ is the Ohmic resistance of the sample. The onset of electromodulated transmission indicates that the CDW state is macroscopically polarized [45] (i.e., strained) at a voltage $V_P < V_T$. Also, the spatial dependencies of $\Delta \theta/\theta$ at different voltages is shown in Fig.(1.12b). For $V_P < V < V_T$, the CDW overcomes pinning in the bulk of the sample but still remains pinned at the contacts. In this case, $\Delta \theta/\theta$, due to the bulk polarization, varies linearly with position, changing sign in the center of the sample. This linear dependence implies that the strain in the CDW state is a linear function of position (i.e., $\partial \phi/\partial x$) below or at threshold. For $V > V_T$ however, the CDW depins at the contacts as well, and the current conversion process occurs at the contacts. Therefore, the additional strains in $\Delta \theta/\theta$ which appear in narrow regions ($\sim 100 \mu$m) near the contacts are associated with phase-slip processes.
needed for current conversion from normal to the CDW current and vice versa [45]. It is obvious that the contact strain becomes more prominent with increasing voltage since phase-slip processes occur with ease at higher voltages.

The open and closed symbols in Fig.(1.12a) show the electromodulated transmission at two positions at the end of the sample. Qualitatively, the difference between these signals is approximately the contact contribution and it is plotted versus $I_{CDW}$ as shown in the inset. The contact contribution is logarithmically proportional to the CDW current $I_{CDW}$, consistent with studies done on NbSe$_3$ in which the rate of phase slip, and therefore $I_{CDW}$ was considered to be an exponential function of the strain [69]. Therefore, the nonlinear current appears to only depend on the contact deformation not associated with the bulk polarization. It was also reported that the contact and the bulk electromodulated transmission signals have different temperature dependence in blue bronze [45]. Below 100 K, both components decrease because the density of quasiparticles which screens the CDW deformation goes down with decreasing temperature. However, above 100 K, the bulk component $\frac{\Delta \phi}{\theta}$ falls rapidly with increasing temperature whereas the contact component $\frac{\Delta \phi}{\theta}$ only falls slowly with increasing temperature, again suggesting that the screening charge depends primarily on the rate of current conversion. The disappearance of the bulk component at higher temperatures suggests that phase-slip processes occur more easily in the bulk with increasing temperature.

In addition to spatial and voltage dependencies, the electro-optic effect in blue bronze exhibits frequency (i.e., frequency of the applied bipolar voltage) dependent behavior.

1.6 Dynamics of the CDW

The model introduced in section 1.2.1 is a model that describes the CDW in its ground state. In order to characterize the properties of CDW systems a number of different contributions to the basic model have to be considered, including Coulomb interactions, interactions with impurities, thermal fluctuations, electron and phonon dispersion, interaction with an external field, interaction with uncondensed free carriers, issues related to commensurability of the CDW with the lattice and the consequences of the three-dimensional character of real systems. (For comprehensive reviews see [1,70]). Depending on the level at which these are introduced into the theory, a number of models of CDW properties have been developed. These various models may bear similar results, but in some instances they are widely different.

Two approaches have been used in order to account for these contributions:

1) Use of Ginzburg-Landau (GL) theory: In spite of the difference between superconductors and CDW conductors, they can be treated using the same Ginzburg-Landau formalism as was proven by Gor'kov [71] and discussed in section 1.2.2. Although the GL equations are rather complicated nonlinear differential equations, they are simpler than microscopic
Figure 1.12: a) Voltage dependence of the electromodulated transmission at $x = 1.02$ mm (end of the sample) (open triangles) and 0.8 mm (closed triangles) respectively, on $K_{0.3}\text{MoO}_3$ at $T = 99$ K; solid curve shows the current-voltage dependence. b) Spatial dependence of the electromodulated transmission at different voltages. Data for successive voltages are vertically offset by 0.5% for clarity. Dashed curves show the approximate bulk strains and shading shows the contact strains. Inset: difference between signals $\frac{\Delta \theta}{\theta}$ (open and closed symbols) as function of the $I_{\text{CDW}}$. Taken from Ref. [8].
or kinetic equations because they contain the macroscopic variables only: the space-time dependent complex order parameter $\Delta(x,t)$, electric field and current. Different problems of the theory of nonequilibrium processes can be analyzed with the help of these equations.

2) Use of Microscopic equations of motion: In this formalism, all the work is done starting from the Fröhlich Hamiltonian. This approach is rather difficult, but it is useful in properly accounting for the interaction with uncondensed carriers, especially for the effects of screening, see [31].

The equations of motion can be further simplified in different limits giving rise to a great variety of phenomenological models. A usual simplification is to consider only the acoustic-like excitations of the order parameter phase, as was originally proposed in [72]. This results in the extensively considered Fukuyama-Lee-Rice Hamiltonian for the dynamics of the CDW phase [35]. At this level, the short range pinning to the impurities [35] and the interaction with external field [36] is introduced in a simple way. In addition, the influence of uncondensed charge carriers through the electromagnetic interaction can be introduced, which is known as the two fluid model of CDW dynamics [36]. Eventually, even this 3-d Hamiltonian can be reduced to a 1-d form through a mean field approximation of the inter-chain coupling which leads to the Larkin Hamiltonian [73].

1.6.1 Phenomenological Model of the phase dynamics

Many problems connected with the CDW dynamics were solved on the basis of phenomenological equations [31]. The CDW is considered as an anisotropic elastic medium moving with friction under the action of an electric field and interacting with the impurities. The expression that governs the phase dynamics according to the Fukuyama-Lee-Rice (FLR) is given by phase [35,36,72]:

$$m^* \frac{\partial^2 \phi}{\partial t^2} + \gamma_0 \frac{\partial \phi}{\partial t} - K \nabla^2 \phi + \sum e n_i V(\mathbf{r} - \mathbf{R}_i) \sin(\mathbf{Q} \cdot \mathbf{r} + \phi) = \frac{e n_c E_x}{Q_x}$$ (1.20)

where $\gamma_0$ is the intrinsic CDW damping, $K$ is the elastic constant, $n_c$ is the CDW condensate density, $m^*$ is the CDW effective mass, the term containing the summation represent the CDW interaction with randomly distributed impurities. It is assumed that the interaction potential is small so it does not lead to modification of the amplitude of the collective mode $n_c$. The electric field $E_x$ is not the applied field but the internal field, and thus subject to screening by the uncondensed carriers, and therefore to spatial and temporal fluctuations [59,74,75]. This fact has very important consequences in setting the value of the damping parameter $\gamma$ at low frequency [76–78]. The applied field $E$ is related to $E_x$ by [56]

$$E_x(r,t) = E - \frac{e n_c}{\sigma Q_x} \frac{\partial \phi}{\partial t}$$ (1.21)
Substituting Eq.(1.21) into Eq.(1.20) leads to an equation with identical form, but with a
applied field $E$ and an enhanced damping constant $\gamma$

$$m \frac{\partial^2 \phi}{\partial t^2} + \gamma \frac{\partial \phi}{\partial t} - K \nabla^2 \phi + \sum e n_1 V(\mathbf{r} - \mathbf{R}_i) \sin(Q \cdot \mathbf{r} + \phi) = \frac{e n_c E}{Q_x}$$

(1.22)

where

$$\gamma = \gamma_0 + \frac{e^2 n_c^2}{\sigma Q_x^2}$$

(1.23)

and $\sigma$ is the lineal conductivity of the normal carriers [79, 80]. Therefore, for the semiconducting CDW systems where the conductivity $\sigma$ has an Arrhenius temperature-dependence, the damping strongly increases with the decreasing temperature.

Equation 1.22 is still rather too complex for efficient numerical simulation and a number of further approximations are conventional: a) The term $m^* \frac{\partial^2 \phi}{\partial t^2}$ is neglected except at very high frequencies. This is possible for frequencies $\ll \gamma/m^*$, which is typically several GHz or higher. b) The impurity interaction is taken to be a $\delta$-function when the behavior on short length scales is not considered. c) Most numerical work is done on one dimensional models, although real systems have three dimensional coherence. This should not be important for qualitative descriptions of the dynamics because a weak impurity interaction is relevant in all dimensions.

A further simplification made by the Cornell group [9] is to substitute the effects of short length scale phase variations associated with impurity pinning for a phenomenological pinning field $E_p$ taken to be a function of $i_c$. For the sample they examined the form of $E_p(i_c)$ was determined experimentally and is shown in Fig.(1.13). Taking into account these assumptions Eq.(1.22) becomes

$$\gamma \frac{\partial \phi}{\partial t} - K \nabla^2 \phi = \frac{e n_c}{Q_x} (E - E_p)$$

(1.24)

This equation determine macroscopic variations of the CDW phase $\phi$ associated with boundary conditions by balancing the forces due to the CDW damping ($\propto \partial \phi/\partial t$), pinning ($E_p$) and elasticity [$\propto K(\partial^2 \phi/\partial x^2)$] with the electric force ($\propto E$). Using $E = r_s i_s$, $i_{\text{total}} = i_c + i_s$, $i_c = A \frac{e n_c}{Q_x} \frac{\partial \phi}{\partial t}$ and $r_c = \gamma \frac{1}{\frac{e n_c}{Q_x}^2}$ Eq.(1.24) can be written as

$$i_c = \frac{1}{r_c + r_s} \left[ r_s i_{\text{total}} - E_p(i_c) + \frac{Q}{e n_c} K \frac{\partial^2 \phi}{\partial x^2} \right]$$

(1.25)

where $r_s$ and $r_c$ are the single particle resistance per unit length and the high-field resistance per unit length respectively. Eq.(1.25) written in terms of the resistivities and CDW current densities yields

$$j_c = \frac{1}{\rho_c + \rho_s} \left[ \rho_s j_{\text{total}} - E_p(j_c) + \frac{Q}{e n_c} K \frac{\partial^2 \phi}{\partial x^2} \right]$$

(1.26)
where \( \rho_s \) and \( \rho_c \) are the single particle resistivity and CDW high field resistivity; \( j_s \) and \( j_c \) denote the single particle current density and CDW current density respectively.

Equations 1.24 or 1.25 or 1.26 derived from the FLR model neglects phase slip process, i.e., the problem of conversion between collective current and single particle current at contacts current is ignored. The problem of current conversion has been an issue of considerable interest [9, 45, 51]. To account for these, the Cornell group [9] incorporated the phase-slip rate term given by Eq.(1.10) into Eq.(1.24)

\[
\frac{\partial \varphi(x,t)}{\partial t} = \frac{Q}{en_c \rho_c + \rho_s} \left[ \rho_s j_{\text{total}} - E_p(j_c) + \frac{Q}{en_c} K \frac{\partial^2 \varphi}{\partial x^2} \right] - \int_{-\infty}^{x} r_{ps}(x',t)dx' \tag{1.27}
\]

where the renumbered phase \( \varphi(x,t) \) is defined as

\[
\varphi(x,t) = \phi(x,t) - \int_{-\infty}^{t} \int_{-\infty}^{x} r_{ps}(x',t')dx'dt' \tag{1.28}
\]

Qualitatively, \( \varphi(x,t) \) describes CDW deformations while \( \phi(x_0,t) \) describes CDW sliding. This is illustrated by the condition for steady state CDW sliding, \( \partial \varphi / \partial t = 0 \), which contrast with the well known relation \( i_c \propto \partial \phi / \partial t \).

Notice that Eq.(1.25) can also be written as

\[
\frac{\partial \epsilon}{\partial x} = -\frac{en_c}{Q^2 K} \left[ \rho_s j_{\text{total}} - E_p(j_c) - (\rho_c + \rho_s) j_c \right] \tag{1.29}
\]

where we have used the definition of strain \( \epsilon = Q^{-1} \partial \phi / \partial x \). In the absence of phase slip, \( j_c \) must equal zero everywhere and the right hand side of this equation is independent of position. The elastic force \( (\propto \partial \epsilon / \partial x) \) is constant between the current contacts, and the CDW strain varies linearly with \( x \) as in Eq.(1.8). If \( r_{ps} \) occurs but is confined to tiny
regions at the current contacts, then \( j_c \) is nonzero but essentially independent of \( x \) between the current contacts. The elastic force is again constant and the strain varies linearly with \( x \). However, their magnitudes are smaller than in the absence of phase slip, since viscous damping for finite \( j_c \) reduces the force available to deform the CDW.

The Cornell group [9] used multi-contact transport measurements to determine the position and time dependence of the strain in NbSe\(_3\) after a current reversal, and simulated their results using the one-dimensional diffusion-like equation given by Eq.(1.27). Table 1.5 shows the parameters used in their simulations.

Table 1.5: Parameters used by the Cornell group [9] in their simulations on NbSe\(_3\): \( L \) is the separation distance between the current contacts, \( \rho_s \) and \( \rho_c \) are the single particle and CDW high field resistivities; \( Q \), \( n_c \) and \( K \) are the CDW wave vector, CDW condensed electron density and CDW elastic constant. The \( r_0 \) and \( \varepsilon_B \) values come from the model for the phase-slip rate \( r_{ps} \) given by Eq.(1.10)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>670 ( \mu m )</td>
</tr>
<tr>
<td>( Q )</td>
<td>0.45( \AA^{-1} )</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>( 8.8 \times 10^{-7} \Omega m )</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>( 3.0 \times 10^{-6} \Omega m )</td>
</tr>
<tr>
<td>( n_c )</td>
<td>( 1.9 \times 10^{-3} \AA^{-3} )</td>
</tr>
<tr>
<td>( K )</td>
<td>( 6.2 \times 10^{-3} \text{eV\AA}^{-1} )</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>( 5 \times 10^{15} \text{m}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( \varepsilon_B )</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The phase and strain profiles are shown in Fig.(1.14) for times \( t = 0, 1, 3, 5, 10, 15, 20, 30, 50, 60, 100, 300 \mu s \). Notice that the strain varies linearly with position in the center of the sample, with extra strains near (\( \approx 100 \mu m \)) the contacts. Measuring changes in infrared transmission, similar behavior of the strain profiles have been observed in K\(_{0.3}\)MoO\(_3\) [29,67].

This phenomenological model captures the results of more microscopic calculations which considered the details of charge conversion and dislocation motion and pinning [51], and reproduced the observed spatial/temporal phase variations of their experiments.

1.7 Physical properties of two CDW materials

1.7.1 Physical properties of K\(_{0.3}\)MoO\(_3\)

K\(_{0.3}\)MoO\(_3\) belongs to the blue bronze family A\(_{0.3}\)MoO\(_3\) (A=K, Rb, Tl), which are quasi one dimensional metals (\( \sigma(300 \text{ K}) \approx 10^4 \text{ (\Omega cm)}^{-1} \)) with a deep blue appearance. The schematic structure of A\(_{0.3}\)MoO\(_3\) is shown in Fig.(??). The structure of the blue bronzes is built up from chains of MoO\(_6\) octahedra, separated by chains of alkali metal atoms, leading to a quasi-one-dimensional electronic band structure. The MoO\(_6\) layers are built by clusters of ten edge and corner sharing octahedra connected by corner sharing along the [010] and [102] directions. The monoclinic unit cell contains two clusters or 20 formula units [10]. The unit cell parameters of the known blue bronzes, A\(_{0.3}\)MoO\(_3\), given in Table 1.6 show
small variations in $a$, $c$ and $\beta$ with A, while the unique monoclinic $b$ axis remains practically unchanged with the increasing size of the A ion. This shows that the the chainlike coupling of the MoO$_6$ octahedra along the $b$ crystallographic directions is unaffected by the nature of the A ion in the blue bronzes. Since the stoichiometry of the blue bronzes is exact, i.e., A$_{0.3}$MoO$_3$, three electrons are transferred to the Mo$_{10}$O$_{30}$ bands to partially fill them. A$_{0.3}$MoO$_3$ has an approximately 3/4 filled conduction band at room temperature [81]. The metallic conductivity of A$_{0.3}$MoO$_3$ for temperatures above $T_P$ is due to the A ions which donate their electrons to the Mo 4d conduction band.

That the blue bronzes undergo a metal insulator transition at 180 K was first reported more than 30 years ago [82]. A more recent reexamination of the resistivity on single crystals of K$_{0.3}$MoO$_3$ showed great anisotropy: $\rho_b : \rho_{[102]} : \rho_{[\overline{2}01]} \sim 0.001 : 0.1 : 1$ at all temperatures [13], as shown in Fig.(1.16). Similar anisotropy of the temperature variation

Figure 1.14: CDW phase and strain profiles simulated by the Cornell group [9]. Current contacts are located at $x = 0$ and $x = 670$ µm indicated by the dotted vertical lines. Profiles are shown for $t = 0$, 1, 3, 5, 10, 15, 20, 30, 50, 60, 100, 300 µs.
of the resistivity is found in the Rb and Tl analogs [83].

The opening of the gap at the Fermi surface is indicated by the metal-insulator transition at 180 K in the temperature dependence of the conductivity as shown in Fig.(1.17). The optical reflectivity data [81], Raman scattering studies [84], magnetic susceptibility [85] and low temperature specific heat [86] support transition to a CDW state in the blue bronzes. The nearly identical $T_P$ values close to 180 K in all of the $A_{0.3}$MoO$_3$ blue bronzes (Table 1.6) indicate that the electronic properties are determined primarily by the MoO$_6$ octahedral network, which is nearly the same in each bronze as evidence by the nearly identical values of the crystallographic $b$ axis.

Both Hall effect [13] (Fig.(1.18a)) and thermopower [13] (Fig.(1.18b)) data show that the dominant carriers are holes above the Peierls transition and electrons below.

Quasi-one dimensional materials with CDWs exhibit also remarkable changes in their thermodynamic properties at the CDW phase transition. Figures 1.19 and 1.20 exemplify these changes. The first figure shows the measurements of the specific heat, thermal expansivity and relative changes in the Young’s moduli (in three crystallographic directions) on K$_{0.3}$MoO$_3$ near its 180 K CDW transition. The latter figure shows the magnetic susceptibility as a function of temperature in the vicinity of the CDW phase transition. All properties were measured on pieces of the same single crystal by Brill at al. [15] and Hauser et al. [14]. It is worthwhile to mention that all quantities were analyzed using the same free energy expression appropriate for a three-dimensional XY model of the transition.

### 1.7.2 Physical properties of NbSe$_3$

NbSe$_3$ has two Peierls transitions, one at $T_{P1} = 142$ K and one at $T_{P2} = 59$ K. NbSe$_3$ is metallic at room temperature and stays metallic at low temperatures since part of the Fermi surface remains ungapped, see Fig.(1.22). The Peierls transitions can be clearly seen

<table>
<thead>
<tr>
<th>Compound</th>
<th>K$_{0.3}$MoO$_3$</th>
<th>Tl$_{0.3}$MoO$_3$</th>
<th>Rb$_{0.3}$MoO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit Cell</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>C2/m</td>
<td>C2/m(?)</td>
<td>C2/m</td>
</tr>
<tr>
<td>$a$(Å)</td>
<td>18.25(1)</td>
<td>18.486(1)</td>
<td>18.94(1)</td>
</tr>
<tr>
<td>$b$(Å)</td>
<td>7.560(5)</td>
<td>7.5474(6)</td>
<td>7.560(5)</td>
</tr>
<tr>
<td>$c$(Å)</td>
<td>9.855(6)</td>
<td>10.0347(7)</td>
<td>10.040(6)</td>
</tr>
<tr>
<td>$\beta$(°)</td>
<td>117.5(1)</td>
<td>118.377(6)</td>
<td>118.8(1)</td>
</tr>
<tr>
<td>$T_P$(K)</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 1.6: Unit Cell Parameters of $A_{0.3}$MoO$_3$ bronze bronzes. Taken from Ref. [10].
in Fig.(1.22) as dips in the temperature derivative of $\ln R(T)$.

The unit cell of NbSe$_3$ is monoclinic and contains six chains, divided into three types. The dimensions of the unit cell are: $a = 10.009$ Å, $b = 3.48051$, $c = 15.629$ Å and $\beta = 109.47^\circ$. The chains are parallel to the crystallographic $b$-axis. The three types can be distinguished by the strength of the outer Se-Se bonds and the spacing between Se atoms in each prism, indicated in Fig.(1.21). Chain III has the closest chalcogen spacing and is associated with the first transition at $T_{P1}$. Chain I, with intermediate chalcogen spacing, is associated with the second transition at $T_{P2}$. Chain II has the largest chalcogen spacing and does not form a CDW.

Typical threshold fields for NbSe$_3$ are 5-50 mV/cm. The threshold field for the second transition is an order of magnitude lower than for the first transition. The room temperature resistivity along the $b$-axis is 1.86 $\Omega\mu$m [2]. Perpendicular to the $b$-axis the room-temperature resistivity of NbSe$_3$ is 10 to 100 times higher [16].
Figure 1.15: The structure of $A_{0.3}\text{MoO}_3$ crystal: a) 3-d representation of the cluster of MoO$_6$ octahedra, b) planar view of the cluster in a), c) planar view of the sheets consisting of the chains of MoO$_6$ clusters sharing only the corners, separated by A atoms, d) 3-d representation of c). Taken from Ref. [10].

Figure 1.16: Temperature dependence of the resistivity on $K_{0.3}\text{MoO}_3$ along the $b$, [102] and perpendicular to $[\overline{2}01]$ directions. Taken from Ref. [11].
1.17: The temperature dependent linear conductivity of $\text{K}_{0.3}\text{MoO}_3$ is shown together with the logarithmic derivative of the conductivity. The dashed line is the activated fit of the conductivity below $T_c$ that gives the half-gap value. Taken from Ref. [12].

Figure 1.18: a) Hall constant of $\text{K}_{0.3}\text{MoO}_3$ as a function of temperature. b) Thermopower of $\text{K}_{0.3}\text{MoO}_3$ as a function of temperature, with the temperature gradient either along $b$ or along [102]. Taken from Ref. [13].
Figure 1.19: a) Specific heat and [102] thermal expansivity [14]; b) relatives changes in Young’s moduli in three directions. Open circles: measured data (50% - 75% of the data points are omitted for clarity); solid curves: 3D XY fits; dashed curves: third order polynomial backgrounds of fits. \( R = 8.31 \, J/molK \). Taken from Ref. [15].

Figure 1.20: Measured magnetic susceptibility minus the Curie-Weiss contribution vs temperature (50% of the data are omitted for clarity). The curves are fits to a 3D XY model defined in [15]. Inset: Measured magnetic susceptibility; the heavy curve shows the Curie-Weiss fit. Taken from Ref. [15].
Figure 1.21: The chain structure of NbSe$_3$. The unit cell of NbSe$_3$ has three types of chains (I, II, III). The darker circles denote the atoms in plane and the brighter circles denote the atoms out of plane. Taken from Ref. [16].

Figure 1.22: a) Resistance versus temperature curve of a NbSe$_3$ sample. b) The $dln(R)/dT$ shows two clear dips at both Peierls transitions. Taken from Ref. [16].

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CHAPTER 2: EXPERIMENTAL PROCEDURES

2.1 Electro-Optic System

The story of the electro optic measurements in quasi-one dimensional materials in our laboratory dates back from 1994. Since then many improvements have been made in the electro-optical system. For a detailed review see Ref. [8]. Currently, the system uses four tunable diode lasers (TDLs) and an infrared microscope that focuses the light coming from the TDLs on to the sample. The microscope allows one to make both reflectance and transmission measurements for both polarizations of the incoming light while a square wave voltage is applied to the sample. The block diagram of the electro-optic system that allow us to make this type of measurements is shown in figure 2.1.

This system consists of mainly four components:

1) Tunable diode lasers: The TDLs are conventionally used for molecular spectroscopy but are also the workhorses for our electro-optic measurements, because their wavelengths can be varied quasi continuously over portions of the infrared spectrum. They are lead-salt semiconductor diodes such as Pb$_{1-x}$Sn$_x$Se (lead-tin-selenide), Pb$_{1-x}$Sn$_x$Te (lead-tin-telluride), and PbS$_{1-x}$Se$_x$ (lead-sulfide selenide) with variable compositions [87]. The laser emission wavelength depends on the alloy composition value $x$ and temperature. Our TDLs cover the spectral range between 400 cm$^{-1}$ and 1200 cm$^{-1}$ or between 25 $\mu$m and 8.33 $\mu$m or between 49.6 meV and 148.9 meV.

All the TDLs operate at cryogenic temperatures, typically between 10 K and 100 K. The properties of TDLs are critically temperature dependent and generally require temperature stability better than a small fraction of a Kelvin [88]. Furthermore, the threshold current for emission is typically a few hundred mA. For these purposes a microprocessor-controlled temperature and current regulation system is used.

On the other hand, TDLs change their lasing properties with time and temperature cycling. Therefore, the laser calibrations have to be checked periodically. If the calibration changed by more than a few cm$^{-1}$, then the laser was recalibrated. For a complete description of the calibration process see Ref. [8]. Figure 2.2 shows a typical calibration curve for #3 laser used in our measurements.

2) IR Microscope: The Thermo-Nicolet Continuum infrared microscope was used for the electro-optic measurements. The light coming from the TDL was focused on the sample using this microscope. The light, polarized along the sample width and with multimode power $\sim 0.1$ mW, was incident (on the face of the sample containing the contacts) through a rectangular aperture into a spot typically 50 $\mu$m along the length of the sample and 80 $\mu$m perpendicular. The light position was measured between the closest edges of the light spot and a metal film contact ($x = 0$), but the contact edges were not always sharp, so the absolute positions are uncertain by $\sim 10$ $\mu$m; in addition, the sample position often drifted
Figure 2.1: Block diagram of the electro-optical system to make electro-reflectance and electro-transmittance measurements.
Figure 2.2: Typical calibration curve for a laser. The solid lines shows a fit to the data.

during measurements by ~ 10 µm.

Figure 2.3 shows a part of the continuum infrared microscope. The typical infrared microscope setup has a an objective spaced above a sample stage with the objective facing downward, and the microscope is operated in transmission mode or reflection mode, depending on the type of measurements to be performed. In transmission mode, the infrared light is directed downward through a mirror, which focuses the light on the sample. Light passing through the sample is collected by the condenser, and the light travels along an optical train to an infrared detector. In a reflectance measurement, the infrared light is directed downward through the objective and light reflected from the sample is collected by the objective and detected as outlined above. (In reflection, half of the objective is used for incident light and the other half for reflected light)

The continuum IR microscope has two photoconductive mercury-cadmium-telluride (MCT) detectors with very high peak detectivity. Both detectors, which are mounted in separate steel dewars, operate at 77 K, requiring the use of liquid nitrogen. The first

\[ \nu = a + bT + cT^2 \]

\[ a = 641.33504 \]
\[ b = 2.8260092 \]
\[ c = 0.014299929 \]

\[ 35 \]

1 The Mercury-Cadmium-Telluride (HgCdTe) detector is a ternary semiconductor composed of a thin layer (10 to 20 µm) with metalized contact pads defining the active area. Photons with energy greater than the semiconductor band-gap energy excite electrons into the conduction band, thereby increasing the conductivity of the material. The wavelength of peak response depends on the material’s band-gap energy and can easily be varied by changing the alloy composition. In order to sense the change in conductivity, a bias current or voltage is required. In general, the responsivity and detectivity of these detectors are a function of bias current and the active size of the element.
Figure 2.3: Part of the infrared microscope. The collimated beams are shown for reflectance and transmission sampling modes.

detector covers the spectral range of 450 cm\(^{-1}\) to 1300 cm\(^{-1}\), with the peak detectivity of \(6.6 \times 10^9\) cm\(\sqrt{Hz}/W\) at 465 cm\(^{-1}\). The second detector covers the spectral range of 600 cm\(^{-1}\) to 3000 cm\(^{-1}\), with the peak detectivity of \(4.4 \times 10^{10}\) cm\(\sqrt{Hz}/W\) at 740 cm\(^{-1}\). The first detector, which covers most of the spectral range of our TDLs from 400 cm\(^{-1}\) to 1200 cm\(^{-1}\), was primarily used for spectral measurements, while the second detector was used for the dynamics measurements, discussed in this thesis.

3) Cryostat: A new cryostat had to be redesigned to make measurements below 77 K (nitrogen temperature). Fig.(2.4) is a schematic diagram of the continuous flow cryostat to cool down the \(\text{K}_{0.3}\text{MoO}_3\) sample. Liquid nitrogen or helium is supplied from a separate storage vessel through an insulated transfer tube. A gas flow (diaphragm) pump and a gas flow controller are used to control the flow of gas through the cryostat. A thermometer and a heater, which are mounted on the heat exchanger and surrounded by a perforated copper radiation shield, were used with a temperature controller to achieve the desire temperature of the sample between 45 K and 300 K. However, the sample temperatures may have been a few degrees warmer because of the incident IR light and Joule heating from the applied currents.

The leads for the thermometer, heater, and sample were heat sunk onto the cold plate and passed through a hermetic feed-through to the outside.

The sample was mounted in vacuum on the cryostat sample holder attached to the heat
exchanger and cooled by conduction. The vacuum was maintained in the cavity of the sample chamber by means of a rotary pump running permanently. Additionally, the rotary pump was attached to a fore-line trap to prevent oil mist from the pump backstreaming into the vacuum chamber.

The cryostat had to be pumped out very well (usually overnight) before the sample was cooled down to the desired temperature. Since thin samples of blue bronze samples are very brittle and fragile, a slow cooling rate of ~1.5 K/min was always used during the sample cooling.

The cryostat have two infrared-transmitting KRS-5 windows (thallium bromoiodide) for optical access and is placed on the sample stage of the IR microscope.

4) Lock-in Amplifiers: For relative changes in transmittance or reflectance, the infrared beam was chopped at \( \Omega = 390 \) Hz and a square-wave voltage of frequency \( f = \frac{\Omega}{2\pi} \) Hz was applied to the sample. The modulated transmitted or reflected signal coming from the microscope detector was sent to a pair of lock-in amplifiers connected in parallel. As reference signals for the lock-in amplifiers we used a square wave of frequency \( f \) provided by the function generator and a signal coming from the chopper at frequency \( \Omega \) respectively. The connection and configuration of the lock-ins was that the ratio of the signals precisely gives \( \frac{\Delta \theta}{\theta} \) or \( \frac{\Delta R}{R} \), even though the transmittance or reflectance were not separately measured precisely [65,66]. Most measurements were made with symmetric bipolar square-waves, for which the changes in transmittance and reflectance are \( \Delta \theta \equiv \theta(+V) - \theta(-V) \) and \( \Delta R \equiv R(+V) - R(-V) \). Some unipolar transmittance measurements, for which \( \Delta \theta \equiv \theta(V) - \theta(0) \), were also made. In both cases, the responses both in-phase and in quadrature with the square-wave were measured.

The lock-in amplifiers were interfaced with a computer through a GPIB (general purpose interface bus) board, i.e., IEEE-488 interface bus. The GPIB bus can transfer information at high rates (nominally 1 Mbytes/s). Quickbasic was used as a programming language to communicate with GPIB devices, including Hewlett-Packard multimeters. Several quickbasic programs were written and others modified for different kinds of measurements e.g., spatial and voltage dependencies of electro-reflectance and electro-transmission; frequency dependence of electro-reflectance and electro-transmission, etc. Most of the long time measurements were completely automated except the ones related to the spatial profiles which were semiautomated, since one needed to manually set the position of the sample with respect to the IR light beam spot. All the data collected were analyzed in Sigma Plot and Origin packages. The writing of some scripts was necessary to streamline data processing.

### 2.2 Preparation and Setup of the sample

\( K_{0.3}MoO_3 \) crystals were provided by Professor R. Thorne’s group of Cornell University. For the electro-optic measurements, single crystal samples with small threshold fields are
Figure 2.4: Schematic diagram of Oxford cryostat [17], modified to fit the microscope.
necessary. Samples with higher threshold fields would require higher voltages to be applied, causing Joule heating problems. Electromodulated transmission experiments require very thin (< 5 µm) samples while electro-reflectance experiments require samples with smooth surfaces. Blue bronze crystals were cleaved with tape to thicknesses of 5±2 µm along the plane parallel to the monoclinic b axis and [102] crystallographic directions. This layered structure cleaves easily along the [201] plane. See Ref. [8] for a full description of the cleaving method. Gold or copper contacts (∼ 500 Å) were evaporated on the ends of the samples so that the resulting lengths between the contacts, in the high-conductivity direction of this quasi-one dimensional conductors, were 0.5 - 1.0 mm, while the sample widths were typically ∼ 0.2 mm. Fine silver wires glued to the contacts with conducting paint acted as both flexible current leads and thermal grounds for the fragile samples which were mounted over ∼ 1 mm holes in sapphire substrates in our vacuum cryostat. The sample was configured for two-probe measurements. A mounting scheme for the electro-optic measurements is shown in Fig.(2.5).

Figure 2.5: Schematic representation of the sample (K\textsubscript{0.3}MoO\textsubscript{3}) mounted on a piece of sapphire substrate for reflection and transmission measurements

2.3 Criteria for a good sample

Apart from the good appearance of the sample surface, I-V measurements showing an increase in resistance associated with the Peierls transition at $T_P = 180$ K, nonlinear transport at lower temperatures with a low threshold field (∼ 100 mV/cm at 77 K) and fairly regular, linear variation of $\frac{\Delta \theta}{\Delta}$ with position when measured with bipolar square-waves was used as a good indication of the sample quality. Samples with irregular spatial dependences presumably contained macroscopic defects (e.g., cracks, grain boundaries) that affected the CDW current flow but were not apparent from visible inspection.
CHAPTER 3: EXPERIMENTAL RESULTS OF THE CDW POLARIZATION DYNAMICS ON BLUE BRONZE

3.1 Introduction

Current conversion between single particle and collective current at the current contacts, in CDW materials carrying current, is believed to occur via phase-slip. Depending upon where exactly this process occurs in the sample determines the strain and CDW current profiles, as discussed in section 1.4. Thus, when phase-slip occurs only near the current contacts, then extra strains extend ($\sim$ 100 $\mu$m) away from the contacts, as obtained by the Cornell group [6,9] carrying out conductivity experiments using nonperturbative contacts along a $\sim$ 1 mm long NbSe$_3$ sample. Their results indicated that strains near ($\sim$ 100 $\mu$m) the current contacts reversed quickly ($\sim$ 10 $\mu$s) after reversing the current, whereas the larger strains in the center took several times longer to change. Subsequently, Brazovskii et al. [51] made spatially resolved x-ray diffraction measurements and directly measured the CDW strains in a 4.1 mm long NbSe$_3$ sample. They observed much larger contact deformations than those deduced by the Cornell group and interpreted them as due to an extreme size effect: the distance between contacts is so short that only a small part of the applied normal current is converted, so that the currents $j_c$ and $j_n$ stay far from their equilibrium values. This group also found that the strains near the center of the sample persisted even when the applied voltage was removed [5,51,54]; these nonequilibrating strains were associated with pinning of CDW phase dislocations [51], discussed further below.

Our group [89] also reported results on the same issue using electro-optical measurements on K$_{0.3}$MoO$_3$ and TaS$_3$ [67]. In particular, if unipolar square-waves, in which the voltage oscillated between zero and a voltage of one sign, were applied, no oscillating signal was generally observed in the center of the sample, and only small ac signals associated with the extra contact strains, were observed [66,68]. That the contact strain oscillates with turning the voltage on and off again indicates its connection to current conversion and phase-slip. The bulk strain, on the other hand, was apparently frozen when the applied voltage was removed, consistent with the persistent strains observed with transport [54] and x-ray [5,51] measurements. An important difference between our K$_{0.3}$MoO$_3$ observations and the x-ray results on NbSe$_3$, [51] however, is that in our case the observed contact signal is much smaller than the persistent bulk signal. While this may be a consequence of the difficulty in preparing non-perturbative Ohmic contacts in blue K$_{0.3}$MoO$_3$, as discussed in section 3.4, it may also reflect the fact that the greater CDW incoherence in K$_{0.3}$MoO$_3$, as compared to NbSe$_3$, makes the bulk strain, associated with poor screening and dislocation line pinning, more dominant.

In order to gain some insight into the CDW dynamics, in this chapter we extend the
previous work and study in detail the CDW polarization dynamics in $K_{0.3}MoO_3$ by applying square waves voltages of different frequency to the sample and measuring the changes in infrared transmittance and reflectance as a function of position, voltage and temperature.

### 3.2 Experimental details

Our measurements are based on the electro-optic effect which was discussed in detailed in section 1.5. At any wavelength, the relative changes in transmittance, $\Delta T$, and reflectance, $\Delta R/R$, are assumed to be proportional to the local CDW strain [45,55].

Three different bronze bronze samples were prepared and mounted for these electro-optical measurements using the method described in section 2.2. The final features of the samples were: thicknesses: 5 ± 2 µm, width ~ 0.2 mm, thickness of gold or copper layer (contacts): ~ 500 Å and; sample lengths in the high conductivity direction: 550, 810 and 990 µm for samples 1, 2 and 3 respectively.

Most measurements were made with symmetric bipolar square-waves, for which the changes in transmittance and reflectance are $\Delta \theta = \theta(+V) - \theta(-V)$ and $\Delta R = R(+V) - R(-V)$. Some unipolar transmittance measurements, for which $\Delta \theta = \theta(V) - \theta(0)$, were also made. In both cases, the responses both in-phase and in quadrature with the square-wave were measured; the frequency-dependent phase shift of the microscope detector electronics was determined with a precision of 2°, possibly slightly affecting results at the lowest frequencies, where the quadrature component becomes much smaller than the in-phase component [67].

### 3.3 Results and Discussion

Figure 3.1 shows the onset voltage for the electro-optical effect, $V_{on}$ (sample 3) and the threshold voltage $V_T$, for non-Ohmic resistance (i.e., non-linear current). The difference, $V_T - V_{on}$, is associated with the "phase-slip voltage" [48] in our 2-probe measurements, for which the same contacts on the ends of the sample are used as current and voltage leads; that is, $V_{on}$ is associated with the onset of CDW depinning and strain in the sample bulk whereas $V_T$ is associated with depinning at the contacts, allowing CDW current to flow, as discussed above. For voltages above $V_T$, additional small changes in transmittance, are associated with the extra strains needed for phase-slip [9].

Thin samples were used to help insure uniform current flow through the sample cross-section. This was checked by comparing the dependence of the electrotransmittance and electro-reflectance on position, voltage, and frequency, as shown in Fig.(3.2). As seen, only the absolute magnitudes of $\Delta \theta/\theta$ and $\Delta R/R$ differed, with $\Delta \theta/\theta \sim 3 \Delta R/R$, but they had the same spatial, voltage, and frequency dependences, indicating that the CDW phase gradient and current were uniform across the sample cross-section, at least on the scale of the penetration
Figure 3.1: Dependence of the dc resistance and relative change in transmittance \( (\nu = 820 \text{ cm}^{-1}) \) for sample 3 at \( T \sim 80 \text{ K} \) on voltage across the sample. The transmission is measured at a point adjacent to a current contact \( (x = 0) \) in-phase with a bipolar squarewave at 25 Hz, for which the quadrature changes are negligible. The low-field ”ohmic” resistance associated with quasiparticle current \( (R_0) \), threshold voltage for non-linear current \( (V_T) \) and onset voltage for the electro-optic response \( (V_{on}) \) are indicated.

depth of the light, typically a few times smaller than the sample thickness [55,66].

Detailed measurements were then made primarily on the transmittance, for which the microscope was less susceptible to mechanical noise than reflectance. For each sample, a wavelength was chosen for which the laser power and electro-transmittance were large. (For a sample with \( \alpha t > 1 \), where \( \alpha \) is the absorption coefficient and \( t \) the sample thickness, the transmittance is given by \( \theta \sim (1 - R)^2 \exp(-\alpha t) \), making the electro-transmittance spectrum sample thickness dependent, as discussed in section 1.5.) The photon energies used were between 775 and 890 \( \text{ cm}^{-1} \), on a broad plateau in the \( \Delta \theta / \theta \) spectrum associated with quasiparticle absorption [66]. Samples were also chosen for having fairly regular, linear variations of \( \Delta \theta / \theta \) with position when measured with bipolar square-waves, as discussed in section 2.3. An example is shown in Fig.(3.3).

An interesting feature of Fig.(3.3), that we observed in most samples, is that the zero crossing of \( \Delta \theta / \theta \), i.e., the position of zero CDW strain, varies with voltage. As discussed further in section 3.4, this suggests that the relative ”quality” of the two contacts varies somewhat with voltage. Also shown in Fig.(3.3) is the spatial dependence when a unipolar square-wave is applied. (Note that the magnitude of the unipolar response is roughly consistent with the deviation from linear spatial dependence near the contact observed for the bipolar response at the same voltage.) As discussed above, the transmittance will only oscillate for applied unipolar voltages for strains which decay when the voltage is removed, and that these ”non-pinned” strains were previously only observed to occur adjacent to the contact [66,68]. Now we observed that there are also small unipolar variations in the center
Figure 3.2: Comparison of the (a) spatial, (b) voltage, and (c) frequency dependences of the electro-transmittance (solid symbols, $\nu = 820 \text{ cm}^{-1}$) and electro-reflectance (open symbols, $\nu = 850 \text{ cm}^{-1}$) for sample 1 at $T \sim 80 \text{ K}$ at the frequencies, voltages, and positions indicated. Both the response in-phase and in quadrature with the driving bipolar square-waves are shown.
Figure 3.3: The spatial dependence of the electro-transmittance ($\nu = 820 \text{ cm}^{-1}$) of sample 1 at $T \sim 80 \text{ K}$ in-phase with bipolar square waves at several voltages at 25 Hz, for which the quadrature response is negligible. The sample was 550 $\mu$m long and the light spot was 50 $\mu$m wide. Each data set is vertically offset by 0.002; the dashed zero-line for each data set is shown, with the voltage given on the right. The solid lines through the data points are for reference only. The open symbols show the response for a positive unipolar square wave (multiplied by 10).
of the sample; similar observations were made for other (but not all – see Fig.(3.12), below) samples. The unipolar spatial dependence shown in Fig.(3.3) suggests that the nonpinned strain may "overshoot", flowing into adjacent regions and leaving them with strains of opposite sign during the "on" half cycle and/or strains of the same sign in the "off" half cycle.

All measurements were at high enough temperature that a) the low-field resistance has activation energy $\sim$ half the gap, indicating that the Ohmic transport is dominated by thermally activated quasiparticles [46], b) the non-Ohmic conductivity is dominated by thermal activation over pinning barriers and only exhibits a single threshold voltage and no hysteresis or switching. [90]

3.3.1 Frequency dependence of bipolar response at $T = 80$ K

We measured in detail the voltage and position dependence of the frequency dependence ($2 \text{ Hz} < \omega/2\pi < 4 \text{ kHz}$) of the electro-transmittance at $T \sim 80$ K for the three samples described in section 3.2, using bipolar square-waves. For bipolar square-waves, the response contains both the bulk, non-equilibrating portion of the strain which would stay pinned at $V = 0$ and the non-pinned, contact strain. For samples 1 and 2, however, the non-pinned component piece was extremely small (e.g., see Fig.(3.3)). It was relatively larger for sample 3, but as discussed in section 3.3.2, still did not affect the fits significantly. We therefore assume that the dynamics of the bipolar response is always essentially that of the non-equilibrating strain and is governed by the pinning and motion of CDW phase location loops [43,51]. Representative data sets at $x = 0$ (adjacent to a contact) and $x = 200 \mu m$ for the three samples are shown in figures 3.4-3.6. The following features, all qualitatively similar to previous measurements by R. Rai [67] on TaS$_3$, can be seen: a) At $x = 0$, the response is essentially relaxational. There is a peak in the quadrature response at the same frequency at which the in-phase response falls; the peak height is roughly half the magnitude of the low frequency in-phase response. b) The relaxation peak moves to lower frequencies with decreasing voltage. c) At $x = 200 \mu m$, the response is smaller and slower than at $x = 0$ for each voltage. d) At high frequencies, the in-phase response becomes inverted, corresponding to a delay in the electro-optical response. This occurs at much lower frequencies for $x = 200 \mu m$ than at $x = 0$. (It is most noticeable at $x = 0$ for sample 1; for sample 3 it is generally out of our frequency window.) e) For some voltages and positions, the quadrature signal becomes inverted at low frequencies. It is clearest for sample 1, where it occurs in some cases for frequencies $> 50$ Hz. For the other two samples, it only occurs for $\omega/2\pi < 10$ Hz, where noise and the difficulty in determining the electronics phase shift makes this inversion less certain. The relaxation and delay, and its strong position dependence, can also be seen in time-averaged oscilloscope traces of the transmitted signal (with the chopper turned off), as shown in Fig.(3.4c), where for sample 1
a delay of \( \sim 70 \mu s \) is observed at \( x = 100 \mu m \) and \( V = 3.6V_{on} \), but the delay is only \( \sim 20 \mu s \) for the same voltage at \( x = 0 \). As for TaS\(_3\), the delayed reversal of transmittance seems to begin ”abruptly“, especially at \( x = 0 \). We do not observe the striking polarity dependence of the delay that was observed for TaS\(_3\) [67], however. Also, the delay time increases much more rapidly as one moves away from the contacts for \( K_{0.3}MoO_3 \) than for TaS\(_3\), indicating that the delay is not, as we suggested in [67], a contact effect, e.g., due to the formation of Schottky barriers at the contacts [46], but is intrinsic to the pinning and repolarization of the CDW.

As shown in figures 3.4, 3.5 and 3.6, we have characterized the relaxation and delay by fitting the complex response to the modified harmonic-oscillator equation [67]

\[
\frac{\Delta \theta}{\theta} = \frac{\Delta \theta}{\theta_0} \left( 1 - \frac{\omega_0^2}{\omega^2} \right) + (-i\omega \tau_0)^\gamma
\]  

(3.1)

Here the inertial term is used to parameterize the delays. The exponent \( \gamma \) allows for distributions in \( \omega_0 \) and \( \tau_0 \); in particular, for overdamped cases \( \gamma < 1 \) corresponds to a distribution of relaxation times\(^1\).

The low-frequency inverted quadrature signal for sample 1, discussed further below, is not included in these fits. The voltage and position dependence of the fitting parameters are shown in Fig.(3.7).

For each sample, the relaxation times increase slightly as one moves away from the contact and for each sample/position, the relaxation time is seen to vary as \( \tau_0 \sim V^{-p} \), with \( p \) between 1 and 2, as for TaS\(_3\) [67]. (We note that while a similar value of \( \tau \sim 1 \) ms at \( V_T \) was deduced for the rate of polarization from an unpolarized state, it had a much stronger, exponential, voltage dependence [93]) Note that the onset of CDW current at \( V_T \) appears to have no affect on the relaxation time. The resonant frequencies tend to weakly \((\sim V^{1/2})\) increase with increasing voltage, but much more striking is the rapid increase in resonant frequency (i.e., decrease in inertia) as one approaches the contact, with the resonant frequency in some cases exceeding our frequency window. The amplitudes decrease rapidly as one approaches \( V_{on} \); away from the contacts, the amplitudes start decreasing again at high voltage whereas they approximately saturate at \( x = 0 \) [45]. Finally, for samples 2 and 3 the exponent \( \gamma \) decreases at small voltages as the resonance becomes increasingly overdamped, indicating that the distribution of relaxation times is becoming broad. For example, \( \gamma \sim 0.9 \) corresponds to a distribution of \( \tau \)’s approximately a half decade wide while \( \gamma \sim 2/3 \) corresponds to a distribution over a decade wide [92]. (This broadening can mask the expected dynamic critical slowing down expected at \( V_{on} \) [94], discussed further in chapter

\(^1\)The overdamped case corresponds to \( \omega_0 \rightarrow \infty \) and the solution given by Eq.(3.1) becomes \( \frac{\Delta \theta}{\theta} = \frac{\Delta \theta}{\theta_0} \left( 1 - \frac{\omega_0^2}{\omega^2} \right) = \int_0^\infty G(\tau) \frac{d\ln \tau}{\tau^3} \) where the distribution of relaxation times is \( G(\tau) = \frac{1}{\pi} \left( \frac{\tau}{\tau_0} \right)^\gamma \sin \theta \left( \frac{\tau}{\tau_0} \right)^{\gamma/2} + 2 \left( \frac{\tau}{\tau_0} \right)^\gamma \cos \gamma + 1 \)

and \( \theta = \arctan \left( \frac{\sin \pi \gamma}{\cos \pi \gamma} \right) \). See [91,92].
Figure 3.4: (a,b) The frequency dependence of the electro-transmittance ($\nu = 820 \text{ cm}^{-1}$) of sample 1 at a few bipolar square-wave voltages at a position (a) adjacent to a current contact and (b) 200 $\mu$m from the contact; both the response in-phase and in quadrature with the square wave are shown. The arrows indicate the high-frequency inverted inphase response associated with delay and the low-frequency inverted quadrature response associated with long-time decay of the electro-optical signal. The curves are fits to Eq.(3.1). (c) Electro-transmittance vs. time for $V = 3.6V_{on}$, $\omega/2\pi = 3.2$ kHz bipolar square wave at two positions; the applied square-wave is shown for reference.
Figure 3.5: The frequency dependence of the electro-transmittance \((\nu = 890 \text{ cm}^{-1})\) of sample 2 at a few bipolar square-wave voltages at a position (a) adjacent to a current contact and (b) 200 \(\mu\text{m}\) from the contact; both the in-phase and quadratures responses are shown. The arrow indicates the high-frequency inverted in-phase response associated with delay for \(x = 200 \mu\text{m}\). The curves are fits to Eq.(3.1).
Figure 3.6: The frequency dependence of the electro-transmittance ($\nu = 820 \text{ cm}^{-1}$) of sample 3 at a few bipolar square-wave voltages at a position (a) adjacent to a current contact and (b) 200 $\mu$m from the contact; both the in-phase and in quadrature responses are shown. The arrow indicates the high-frequency inverted in-phase response associated with delay for $x = 200 \mu$m. The curves are fits to Eq.(3.1)
Figure 3.7: Voltage dependence of fitting parameters for Eq.(3.1) for sample 1 (open symbols), sample 2 (black symbols), and sample 3 (grey symbols) at $T \sim 80$ K: a) relaxation times, b) resonant frequencies, c) amplitudes, d) exponents. The triangles are for $x = 0$, diamonds for $x = 100$ µm, and squares for $x = 200$ µm. Reference lines showing $1/V$ and $1/V^2$ behavior are shown in (a) and $V^{1/2}$ behavior in (b). The vertical arrows in (a) indicate the non-linear current threshold voltages. In (c), the curves are guides to the eye, with extrapolated arrows showing the onset voltages.
5) At any given voltage, or depinning force \((V - V_{on})/L\) or \((V - V_T)/L\), sample 2 is much slower than samples 1 or 3; e.g., its relaxation times are over an order of magnitude larger and resonant frequencies an order of magnitude lower. (The time constants for samples 1 and 3 are close to those of TaS₃ [67].) As we’ll discuss in section 3.3.2, this suggests that sample 2 is effectively "colder" than the other samples so that the CDW current density is less for a given driving force. Our preliminary data on sample 2 suggested that this was so but, unfortunately, the sample broke before measurements could be made at different temperatures or larger currents. (Note that the threshold and onset electric fields for sample 2 are close to that of the shorter sample 1 but much greater than those of sample 3.) The inverted quadrature signal observed at low frequencies, especially for sample 1, corresponds to a long-time decay of the electro-optic response. (The small magnitude of this decay and poor signal/noise ratio of low-frequency oscilloscope measurements prevented us from directly observing this decay in a time trace like that of Fig. 3.4c.) Since \(\gamma \sim 1\) for sample 1, the response could be fit by including a term \(i\Omega_x^2\gamma_0/\omega\) in the denominator of Eq. (3.1), where \(\Omega_x\) is the frequency at which the quadrature signal changes sign. However, \(\Omega_x\) had no clear position or voltage dependence, so the fits are not shown. Furthermore, the significance of the decay is not clear. It should be emphasized that this decay is observed for bipolar square waves, including cases for which \(|V|\) is always above threshold, so is not due to the slow decay of bulk strains at \(V = 0\) [51]. In the Cornell model, the elastic force on the CDW (the gradient of the strain) does decay with time but no decay is expected for the strain itself [9], as discussed in chapter 4.

3.3.2 Temperature dependence of time constants

The dynamics of many properties associated with CDW pinning/depinning are governed by the density of quasiparticles [95], and hence time constants are thermally activated for semiconducting materials. The dielectric constant, associated with small oscillations of the CDW about its pinning configuration, is a very prominent example [96]. The magnitude of strain for a given voltage, since it depends on screening by quasiparticles, is also expected to be activated, and indeed the magnitude of the electrotransmittance at \(V_T\) was observed to be activated at low temperatures [29]. On the other hand, in the Cornell model, the rate of change of strain, when reversing the current, is governed not only by the magnitude of the strain (near the contacts) but by the CDW current [6,9]. It was therefore interesting to study the dynamics of the electro-transmittance at different temperatures to see how these different factors are manifested. Measurements were made on sample 3 for temperatures between 45 K and 100 K. (The decreasing resistance prohibited measurements at voltages much above threshold at higher temperatures, while the decreasing magnitude of the electro-transmittance prevented frequency dependent measurements at lower temperatures.) To make comparisons of the response at different temperatures, we had to decide on
an appropriate voltage criterion. Both the onset and threshold voltages \([25]\), as well as their
difference, decrease with decreasing temperature in this range, so temperature-dependent
comparisons at a constant voltage are not appropriate. Figure 3.7 also shows that the \([68]\)
relaxation time does not change as the voltage passes through \(V_T\) (and hence must also have
a weak dependence on CDW current here). Therefore, we chose as our criterion fixed values
of \(V - V_{on}\), approximately proportional to the average driving force on the strain and CDW.
(The pinning force, in fact, depends on the voltage and CDW current for small currents \([9]\))
Fig.(3.8) shows the temperature dependence of the parameters of Eq.(3.1) for two driving
voltages, \(V = V_{on} + 10 \text{ mV} \) and \(V = V_{on} + 20 \text{ mV}\), and two positions, \(x = 0\) and \(x = 200 \mu\text{m}\).
Also shown is the temperature dependence of the low-field, quasi-particle resistance
and conductance. For each position/voltage, the magnitude of the electrotransmittance
varies roughly as the conductance for \(T < 70 \text{ K}\) and saturates at higher temperature, as we
previously observed \([29]\). In contrast, for each data set the relaxation times and resonant
frequencies have a weaker temperature dependence, with activation energies approximately
half that of the conductance.

However, the CDW current for each voltage, defined as \(I_{CDW} = I_{total} - \frac{V}{R_0}\), was observed
to also have this smaller activation energy. We therefore plotted the relaxation times and
frequencies vs. \(I_{CDW}\), as shown in Fig.(3.9). \((I_{CDW}\) is plotted vs. voltage in the inset to
Fig.(3.9); for this sample, \(I_{CDW} \approx (V - V_T)^{3/2}\) \(I_{CDW}\) for each voltage/position, \(\tau_0\) and \(1/\omega_0\)
scale roughly as \(1/I_{CDW}\); that is, for a given driving force and position, the dynamical rates
are proportional to the CDW current. We should emphasize that this dependence on CDW
current only occurs for a given driving voltage; the relaxation rates themselves are not simply
functions of \(I_{CDW}(T)\), even for large CDW currents. This is shown in Fig.(3.10), where
we plot the fit parameters of Eq.(3.1) for fixed \(I_{CDW} = 100 \mu\text{A}\). While the temperature
dependence of the rates are weaker than for fixed driving voltage, they are still strongly
temperature dependent. To check this dependence of the dynamical rates on driving voltage
and CDW current, we did temperature dependent measurements on an additional sample.
For sample 4 \((L \sim 960 \mu\text{m})\), the fits to Eq.(3.1) were not as good as for the other samples,
especially at the highest and lowest frequencies, but the fits at intermediate frequencies were
sufficient to determine relaxation times. As shown in the inset to Fig.(3.11), the relaxation
times for this sample tended to saturate at low temperatures, very different behavior from
sample 3. Nonetheless, as shown in Fig.(3.11), there is still a linear dependence, for each
voltage/position, between the relaxation rate and CDW current.

### 3.3.3 Frequency dependence of contact strains

For most samples, the contact strain measured with unipolar square-waves above thresh­
old has been too small for frequency dependent measurements. An exception was sample
3, for which the spatial dependence of the unipolar \((V = 2V_T)\) and bipolar \((V = 1.5V_T)\)
Figure 3.8: Temperature dependence of frequency-dependence fitting parameters for Eq.(3.1) for sample 3 ($\nu = 820 \text{ cm}^{-1}$) for two positions and voltages, as indicated: a) relaxation times, b) resonant frequencies (only determined for $x = 200 \text{ } \mu \text{m}$), c) amplitudes, d) exponents. The curves in (a,b,c) show the temperature dependence of the low-field resistance and conductance.
Figure 3.9: Relaxation times and resonant frequencies for sample 3 ($\nu = 820 \text{ cm}^{-1}$) plotted as functions of the temperature dependent CDW current at $V = V_{\text{on}} + 10 \text{ mV}$ and $V_{\text{on}} + 20 \text{ mV}$. A line with slope = 1 is shown for reference. Inset: CDW current vs. voltage at a few temperatures. Note that $V_T - V_{\text{on}}$ increases from 3 to 8 mV with increasing temperature.
Figure 3.10: Temperature dependence of frequency-dependence fitting parameters for Eq.(3.1) for sample 3 ($\nu = 820 \text{ cm}^{-1}$) for $I_{\text{CDW}} = 100 \mu\text{A}$ and two positions: a) relaxation times, b) resonant frequencies (only determined for $x = 200 \mu\text{m}$), c) amplitudes, d) exponents.
Figure 3.11: Relaxation times for sample 4 (\(\nu = 775 \text{ cm}^{-1}\)) plotted as functions of the temperature dependent CDW current at \(V = V_{\text{on}} + 10 \text{ mV}\) and \(V_{\text{on}} + 20 \text{ mV}\). A line with slope = 1 is shown for reference. Inset: Temperature dependence of the relaxation times.
responses at \( T = 101 \text{ K}, \ \omega/2\pi = 25 \text{ Hz} \) are shown in the inset to Fig.(3.12). For this sample, the unipolar response disappears away (> 200 \( \mu \text{m} \)) from the contacts. Figure 3.12 shows the frequency dependence of the bipolar response and both the positive and negative unipolar responses at 101 K, \( 2V_T \), and \( x = 0 \). The parameters for the fits to Eq.(3.1) are listed in Table 3.1. Note the following features:

1. The negative unipolar response is larger than the positive, as our group previously observed [68]. Polarity dependent strains have also been observed in NbSe\(_3\) and are not understood [6,51].

2. Pronounced [55] relaxation peaks in the quadrature response are not observed for unipolar excitation. In fact, the unipolar response can be fit to Cole-Cole relaxation. (see footnote on page 46 and references [91,92], as shown in the Table 3.1, with a very small \( \gamma = 0.65 \), implying a decade wide distribution in relaxation times [92], which effectively washes out the relaxation peak.

3. Given this wide distribution in \( \tau \)'s, the differences in relaxation times between the bipolar and unipolar responses is probably not significant. Indeed, it is striking that the "non-pinned", contact unipolar response is not much faster than the (mostly nonequilibrating) bipolar response. This would suggest that changes in the contact strains, as the CDW current is turned on and off, also involves the motion of phase dislocation loops. These loops may be smaller than those pinning the bulk polarization, and may also be able to move longitudinally (i.e., glide) into the contacts as well as transversely (climb) across the sample, accounting for the differences in the dynamic response. Also shown in Fig.(3.12) is the bipolar response at \( x = 200 \mu \text{m} \), where the unipolar response is zero. As usual, the striking difference between the response here and at the contact is that the resonant frequency has moved well into our window; in fact the resonance at \( x = 200 \mu \text{m} \) is underdamped even though the relaxation time (see Table 3.1) has also increased considerably. In Reference [45], it was speculated that the faster bipolar response at the contact vs. the interior might be due to the fact that at the contact the bipolar response comes from both non-pinned and non-equilibrating strains, whereas the response in the interior only comes from non-equilibrating strains. However, the difference between the bipolar and two unipolar responses, also shown in Fig.(3.12), gives the \( x = 0 \) non-equilibrating response only. This difference was also fit to Eq.(3.1) and its parameters listed in Table 3.1. The difference response is only slightly slower (i.e., relaxation time is essentially the same and resonant frequency only slightly smaller) than that of the full bipolar response, showing that the dynamics of the bipolar response is essentially determined by that of the non-equilibrating part of the strain, even at points adjacent to the contact.
Figure 3.12: The frequency dependence of the electro-transmittance ($\nu = 820 \text{ cm}^{-1}$) of sample 3 at $V = 2V_T = 3.1V_{on}$ and $T = 101 \text{ K}$. Shown are the measured in-phase and quadrature responses for bipolar square-waves at $x = 0$ and $x = 200 \mu\text{m}$ and positive and negative unipolar square-waves at $x = 0$. Also shown is the difference between the $x = 0$ bipolar and (difference of the) unipolar responses. The curves are fits to Eq.(3.1). Inset: The spatial dependence of the (in-phase) bipolar ($V = 1.5V_T$) and negative unipolar ($V = 2V_T$) responses at 25 Hz, for which the quadrature responses are negligible.
Table 3.1: Comparison of Eq. (3.1) fit parameters (see Fig.(3.12)) for different squarewaves with \( V = 2V_T = 3.1V_{on} \) for sample 3 at \( T = 101 \text{ K} \)

<table>
<thead>
<tr>
<th>Square-wave/position</th>
<th>( \frac{\Delta \rho}{\sigma} ) 0 (%)</th>
<th>( \tau_0 ) (ms)</th>
<th>( \frac{\omega_0}{2\pi} ) (kHz)</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bipolar, ( x = 0 )</td>
<td>1.05%</td>
<td>0.15</td>
<td>4.70</td>
<td>0.98</td>
</tr>
<tr>
<td>+Unipolar, ( x = 0 )</td>
<td>0.15%</td>
<td>0.053</td>
<td>( \infty )</td>
<td>0.65</td>
</tr>
<tr>
<td>-Unipolar, ( x = 0 )</td>
<td>-0.23%</td>
<td>0.13</td>
<td>( \infty )</td>
<td>0.65</td>
</tr>
<tr>
<td>Bipolar, ( x = 200 \mu m )</td>
<td>0.49%</td>
<td>0.46</td>
<td>0.55</td>
<td>0.94</td>
</tr>
<tr>
<td>Bip.- [(+uni.) - (-uni.)], ( x = 0 )</td>
<td>0.70%</td>
<td>0.16</td>
<td>2.92</td>
<td>1.06</td>
</tr>
</tbody>
</table>

3.4 Summary and Discussion

We used measurements of the changes in infrared transmittance when squarewave voltages are applied to the sample to determine the position, voltage, and frequency dependence of CDW strains (i.e., phase gradients) in K$_{0.3}$MoO$_3$. This technique has the advantage of being able to probe the interior of the sample without placing multiple probes, which can perturb the CDW, on the sample, which has hindered transport measurements of the CDW strain in semiconducting CDW materials [46]. Of course, it is still necessary to place contacts on the ends of the sample, and the largest changes in dynamical properties occur near \( (\sim 100 \mu m) \) these contacts. Important questions, therefore, are to what extent these contacts are equipotentials with minimal band-bending, e.g., due to formation of Schottky barriers in the CDW state [46], and to what extent current enters the sample from the edges of the contacts and quickly distributes through the cross-section. The very small contact strains observed for some samples and the fact that the bulk strain, while varying approximately linearly with position in the sample, is not symmetric on the two sides of the sample with a voltage dependent asymmetry (e.g., see Fig.(3.3)) certainly suggest that our contacts are "imperfect". Indeed, the longitudinal length-scale with which current is expected to spread through the sample cross-section from surface contacts is [46] \( \lambda \sim \eta^{1/2} \), where \( \eta \) is the ratio of longitudinal and transverse conductivities. For blue bronze, \( \eta \sim 1000 \) [97], making \( \lambda \) comparable to the length scale of measured changes at the contacts. However, the fact that the electro-transmittance (probing the whole sample crosssection) and the electroreflectance (probing only the \(< 2 \mu m \) penetration depth [55, 66]) have the same spatial and frequency dependence (Fig.(3.2)) suggests that current spreading is not a significant problem for our contacts. (Note that the spatial dependence of the electro-reflectance is different for thicker samples [65].) Two possible reasons are that sample defects effectively distribute the current through the cross-section in a distance shorter than \( \lambda \) or that, because the contacts are over 100 \( \mu m \) long, the current actually spreads below them. The rapid varia-
lation of our measured relaxation times and resonant frequencies near the contacts suggests that the first effect is dominant. In fact, the expected length scale for the contact strain is determined by the single particle diffusion length and is expected to be $\sim 100 \, \mu m$, [51] consistent with our measurements. We therefore assume that the edges of our contacts do approximate the locations of CDW current injection reasonably well, so that the relatively small contact strains we measure are not artifacts of poor contacts but intrinsic, e.g., due to the incoherence of the CDW and strong pinning of dislocation lines.

Most of our measurements were for the oscillating response to symmetric bipolar square-wave voltages, so that the CDW strain is oscillating between two opposite configurations. In this case, the oscillating strain has contributions from both the bulk polarization which, due to pinning of CDW dislocations, does not decay in zero field, and a non-pinned strain associated with current conversion, but the latter is small and does not significantly affect the overall frequency dependence. For large voltages, the electro-optic response can be fit as a damped harmonic oscillator, with the resonant frequency corresponding to a delay with respect to the applied square-wave voltage. The delay times increase rapidly between $x = 0$ (the contact) and $x = 100 \, \mu m$ and then continue increasing (by $50 - 100\%$) between $x = 100$ and $x = 200 \, \mu m$. This spatial variation indicates that the delays are intrinsic to the CDW (i.e., not associated with contact barriers [67]) and suggests that the signal driving the strain relaxation effectively flows out of the contact. In this case, the delays we observe near the contacts would be a consequence of our finite spatial resolution. Similarly, in their measurements on NbSe$_3$, the Cornell group found that there was a delay $\sim 10 \, \mu s$ for changes in the electric field, and therefore the strain, in the center of the sample, but no delay at the contacts, and simulated these effects in terms of a strongly strain (and therefore position and voltage) dependent phase-slip rate, presumably reflecting the pinning and motion of dislocation lines [9]. We elaborate on these simulations in chapter 4. In our case, the resulting typical ($T = 80 \, K$) propagation velocity of $\sim 100 \, \mu m/100 \, \mu s$ is comparable to that observed for voltage pulses [98] but orders of magnitude larger than the drift velocity of the CDW, [25] whose motion is limited by scattering with quasiparticles [26]. If we model the CDW strain propagation as a wave on a stretched wire with tension (per electron) $\sim e(V - V_{on})/L \sim 10eV/m$ (consistent with the observed $\omega_0 \sim V^{1/2}$ behavior at large voltages), then a velocity of $1 \, m/s$ corresponds to a reasonable effective mass density for the strain wave of $\sim 1 \, QM_F$, where $Q$ is the CDW wavevector and $M_F$ is the Fröhlich mass ($\sim 300m_e$, Ref. [99]) associated with CDW motion [26]. Of course, this simple result should only be considered order of magnitude and needs to be qualified to account for the strong sample and temperature dependence of the delays. In chapter 4, we also show that in simulations, $1/\omega_0$ does not vary linearly with $x$.

The relaxation time also increases as one moves away from the current contact. For any position in the sample, the average relaxation time $\tau \sim V^{-p}$, with $p$ between 1 and 2.
No structure is observed in \( \tau \) near \( V_T \), where the CDW is depinned at the contacts and dc CDW current can flow. The dynamics are governed both by the force on the CDW (e.g., \( V - V_m \)) and the CDW current. For a given force and position in the sample, both the relaxation and delay times are inversely proportional to the CDW current as temperature is varied. The temperature dependent screening of the quasiparticles directly affects the amplitude of the electro-optic response [29, 55], but it only appears to affect the dynamics through its influence on the CDW current, so that while the response slows with decreasing temperature, it does not slow as much as expected from the quasiparticle density.

Near \( V_T \) at \( T \sim 80 \) K, the typical relaxation time is 1 ms, more than three orders of magnitude greater than the dielectric response time governing small amplitude oscillations of the pinned CDW [100, 101], indicating that repolarization requires large scale rearrangements of the CDW phase. Near \( V_T \) the dynamics are essentially governed by CDW diffusion, not phase-slip, as discussed in chapters 4 and 5, but even for relatively large voltages and phase-slip rates, the relaxation time is slow (e.g., \( \tau > 100 \) \( \mu \)s), suggesting strain relaxation involves the motion of extended defects in the CDW. The measured changes in phase and the simulated changes discussed in chapter 4 may be a coarse grained average of a more complicated phase landscape in which regions of the CDW with equilibrium wave vector are separated by localized, soliton like defects [53, 63, 95]. These presumably accumulate on neighboring chains to form extended defects, such as CDW phase dislocation loops [43, 44, 53, 63]. As mentioned above, in Ref. [51] the pinning of the dislocations was considered to be the cause of persistence of the bulk strains when \( V = 0 \). If so, polarization current would require the lateral motion of these defects along the conducting chains, e.g., glide of the dislocations [63], in contrast to the growth of the loops by climb perpendicular to the chains, responsible for phase slip [43, 44, 53, 96]. As mentioned above, a similar mechanism would hold for the changes in the contact strains, but the wider distribution of relaxation times might indicate a broader distribution of dislocation loop sizes near the contacts where phase slip is also occurring.

For low voltages, the simple damped harmonic fits break down (for most samples), and the response requires a distribution of time constants, which we have parameterized with the exponent \( \gamma \). This may reflect inhomogeneous CDW pinning (and current, when above \( V_T \)) on a length scale much smaller than our typical 50 \( \mu \)m light spot. As mentioned above, this broadening may mask any possible dynamic critical slowing down at \( V_m \) [94]. However, sample 1 did not exhibit this broadening, at least for \( V \sim V_T \), and it showed some evidence of critical behavior at lower voltages; unfortunately, the sample broke before the low voltage range could be investigated well. Since the presence of dynamic critical behavior at depinning has long been an open question that has generated much interest [102], we continued measurements on crystals at low voltages, to be discussed in chapter 5.
CHAPTER 4: SIMULATION OF CDW STRAIN DYNAMICS

4.1 Introduction

In chapter 3 we studied experimentally the CDW polarization dynamics in K_{0.3}MoO_3, which remain semiconducting in the CDW state, by applying squares waves voltages of different frequencies to the sample and measuring the changes in IR transmittance proportional to the CDW strain. The frequency dependence of the electro transmittance was fit to a modified harmonic oscillator response and the evolution of the parameters as a function of voltage, position and temperature was discussed.

On the other hand, the Cornell group [9] studied the time dependence of the CDW strain to one current pulse on NbSe₃, which remains metallic in the CDW state, both experimentally and by modeling their results using a simplified version of the Fukuyama-Lee-Rice [35] model.

In order to gain insight into the CDW strain dynamics, we extended the Cornell work by simulating the CDW strain dynamics on NbSe₃ in response to finite square waves. Consequently, the frequency domain response of the CDW strain response could be obtained and a qualitative comparison with the K_{0.3}MoO_3 results made. In addition, we analyzed the effects of different boundary conditions on the dynamics of the strain.

In this chapter we present the results of our simulations and the corresponding analysis.

4.2 Model

The Cornell group [9] used multi-contact transport measurements to determine the position and time dependence of the strain in NbSe₃ after a current reversal, and simulated their results using a one-dimensional diffusion-like model for the phase. The model was discussed in detail in section 1.6.1. The equation used was

\[
\frac{\partial \varphi(x,t)}{\partial t} = \frac{Q}{en_e} \frac{1}{\rho_c + \rho_s} \left[ \rho_s j_{\text{total}} - E_p(j_c) + \frac{Q}{en_e} K \frac{\partial^2 \varphi}{\partial x^2} \right] - \int_{-\infty}^{x} r_{ps}(x',t)\,dx'
\]  

(4.1)

where CDW \( \rho_c \) and \( \rho_s \) are the high field CDW and single particle resistivities, \( K \) the CDW elastic constant, and \( j_{\text{total}} \) is the total current density, i.e. \( j_{\text{total}} = j_c + j_s \) where \( j_s \) is the single particle current density. The term \( r_{ps} \) represents the phase slip rate given by Eq.(1.10).

In this simplified model, the randomly distributed impurities have been replaced by a phenomenological pinning field, which may depend on CDW current, as discussed below.

For a square-wave current of a given frequency \( \omega \) and amplitude, Eq.(4.1) was solved with \( \varphi = 0 \) everywhere initially and repeating the current reversals until the phase variation becomes periodic in time with \( \varphi(x,t) = -\varphi(x,t + \pi/\omega) \). For each time step \( (\Delta t << 1/\omega) \), Eq.(4.1) was first solved without the phase slip term, which was then added. Finally,
to mimic frequency-dependent lock-in amplifier measurements of electro-optic signals, we calculated the fundamental term (in-phase and in quadrature with the applied square wave) in a Fourier series expansion of the time dependence. For concreteness, Eq.(4.1) was solved using the same parameters as used by the Cornell group [9] for NbSe$_3$ shown in Table 1.5. The extension to parameters appropriate for K$_{0.3}$MoO$_3$ will be discussed later.

For each frequency, the strain profile was found for two different boundary conditions:

1. "Free contacts": We assumed that the CDW phase was not fixed at the current contacts; this is appropriate for the very short non-perturbative side contacts used by the Cornell group [9] who showed that in such a case phase slip extends for $\approx 100$ $\mu$m beyond the contacts. For this case, we fixed the phase at zero at a point $d \geq 100$ $\mu$m beyond the contact (the results did not depend on the choice of $d$).

2. "Pinned contacts": We assumed that the CDW phase was pinned at zero at the current contacts; this would be appropriate for strongly perturbative contacts, such as end contacts or long electrically shorting side contacts, such as those used in our electro-optics experiments [45, 103, 104].

The Cornell group also showed that for their sample, the pinning field varied with CDW current, with a minimum value of 17 V/m for $j_c = 0$, corresponding to a depinning threshold current density $j_T = 1.8 \times 10^7$ A/m$^2$, and increasing rapidly with CDW current, saturating at $\approx 3.50$ mV/m for $j_c > 2j_T$ as can be seen in Fig.(1.13). We solved for the strain profiles with this $E_p(j_c)$ but also examined the consequences of having such a variable $E_p$ by solving for the case $E_p = \text{constant} = 17$ V/m.

4.3 Results and Discussion

In general, the solution of the partial integro-differential equation Eq.(4.1) had to be found numerically; see C for a description of the method used. However, in order to gain insight into the solution of Eq.(4.1), I also solved it analytically without including the phase-slip term $r_{ps}$ for the case of pinned contacts and pinning field $E_p$ equal constant, in which case Eq.(4.1) is the diffusion equation.

4.3.1 Special case: Pinned Contacts, $r_{ps} = 0$ and $E_p = \text{constant}$

This situation corresponds to very low currents where $r_{ps} \sim 0$. In this case the solution can be expanded in a spatial Fourier series, (see A). The in-phase and quadrature responses of the first harmonic of the strain are given by equations Eq.(A-17) and Eq.(A-18) which we rewrite here as

$$
(\varepsilon_{\omega})_{\text{In-Phase}} = \frac{8F\tau_0}{QL\pi} \sum_{n=odd}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L} x \right) \times \frac{1}{[1 + (\omega \tau_n)^2]} \tag{4.2}
$$
\[
(\varepsilon_\omega)_{\text{Quadrature}} = -\frac{8F\tau_0}{QL\pi} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L} x \right) \times \frac{\omega\tau_n}{[1 + (\omega\tau_n)^2]}
\]

where \( F = \frac{Q}{en_c \rho_c + \rho_s} [\rho_s : j_{\text{total}} - E_p] \). The relaxation time of the \( n^{th} \) spatial Fourier component \( \tau_n \) and the diffusion constant \( D \) are given respectively by

\[
\tau_n = \frac{\tau_0}{n^2} = \frac{L^2}{D\pi^2 n^2}
\]

and

\[
D = \left( \frac{Q}{en_c} \right)^2 \frac{K}{\rho_c + \rho_s}
\]

with \( n \) an odd number.

From equations 4.2 and 4.3 is clear that:

1. The response at a fixed position along the sample is strictly speaking not a single relaxational process. On the contrary, it is the sum of multiple relational processes of different amplitudes and relaxation times \( \tau_n \). These amplitudes and relaxation times becomes smaller and smaller for large values of \( n \).

2. The value of \( \omega \) for which the quadrature response is maximum, is independent of the current density \( j_{\text{total}} \). Hence, phase-slip is essential to obtain an amplitude dependent relaxation time.

3. From the graphs of these functions for different number of terms in the summations (see Fig.(4.1)), we immediately see that the higher spatial components have negligible effect on the quadrature response, but enhance the low-frequency in-phase response (by \( \approx 20\% \)).

### 4.3.2 General case: Different Boundary Conditions, \( r_{ps} \neq 0 \)

The inset to Fig.(4.2) shows the spatial dependence of the strain for pinned contacts with constant \( E_p \) for 12.5 kHz and 3.0 kHz square waves of amplitude \( j_{\text{total}} = 3j_T \) immediately after reversing the current, before the strain has a chance to change. (The spatial dependence is shown for half the sample’s length, since the strain is antisymmetric about the center of the sample.) At the lower frequency, this "initial" strain has the expected spatial dependence; i.e. it varies linearly with position near the center of the sample, with extra strain near the contact [9,45]. At the higher frequency, however, the strain stays small for a large region near the center of the sample, as if the strain doesn’t have sufficient time to flow from the contacts to the center [103].
At $t = 0$, the strain has its expected spatial dependence: it varies approximately linearly with position near the center of the sample, with enhanced strains near ($\approx$100µm) the contacts, where most phase-slip occurs. The spatial dependence starts changing immediately at the contacts, but much more slowly with increasing $x$, as also observed by the Cornell group. In particular, away from the contact (Fig.(4.2c), Fig.(4.2d)), the magnitude of the strain increases briefly before it begins its reversal. This "delay" time in the strain reversal increases with $x$.

The effect of variable $E_p$ is to slightly decrease the strain in the phase-slip region, as expected, but does not significantly affect the time evolution of the strain. This was the case for all frequencies and currents examined, so for the remainder of the paper we will discuss only the simpler $E_p = \text{constant}$ results.

The boundary conditions at the contact cause larger differences. From the spatial dependence, one sees that allowing phase slip beyond the contacts reduces the strain, as expected. More surprisingly, this outside phase slip has the effect of slowing the strain reversal between the contacts. This is most dramatic in the vicinity of the contacts.

The frequency dependence of the strain, $\varepsilon_\omega$ for a few currents and two positions, is shown in Fig.(4.3). For each case, the filled symbols are for pinned contacts and the open symbols are for free contacts; note that, in every case, the changes in response are slower for free contacts.

At $x = 0$, (Fig.(4.3a)) the response is essentially relaxational, with a peak in the quadrature response coinciding with the shoulder of the in-phase response, and the relaxation time $(1/\omega_{\text{peak}})$ decreases with increasing current, as we observed in the electro-optic experiments.
Figure 4.2: Dependence of strain on the distance from a current contact \( (x) \) and time after a current reversal for a \( j_{\text{total}} = 3jT \), 12.5 kHz square-wave. (a) position dependence at three times; (b,c,d) time dependence at three positions. Dashed curves: pinned contacts, \( E_p \) = constant; solid curves: free contacts, \( E_p \) = constant; long-short dashed curves: free contacts, \( E_p \) variable. Inset: Comparison of initial \( (t = 0) \) spatial dependencies for 12.5 kHz and 3.0 kHz square waves \( (j_{\text{total}} = 3jT, \text{pinned contacts, } E_p = \text{constant}) \).
Figure 4.3: Frequency dependence of the strain at (a) adjacent to a current contact and (b) 200 μm away, for three values of $j_{\text{total}}$. The top panels show the responses in-phase with the applied square-waves and the bottom panels show the quadrature responses. Solid symbols correspond to pinned contacts and open symbols to free contacts (both with $E_p = \text{constant}$). The dashed curves show fits for the pinned contact cases to Eq.(4.6)
on blue bronze [103, 104].

Note, however, that the magnitudes of the quadrature peaks are less than half the magnitudes of the in-phase responses at low-frequencies; this is true even at very small currents where phase-slip becomes negligible and the response is essentially diffusive. As discussed above, this results in an enhanced in-phase response of the higher spectral Fourier component.

Away from the contact (Fig.(4.3b)), the in-phase response becomes inverted at high frequency, corresponding to the delayed response discussed above. The delay time increases with decreasing current, also as we observed for blue bronze [103]. It is also greater for free contacts than pinned contacts, consistent with the outside phase-slip slowing the overall response.

4.3.3 Variation of the fitting parameters with current

To parameterize these curves, I fit them to the modified harmonic oscillator expression that we used for the electro-optic response in the previous chapter (see Eq.(3.1))

\[ \varepsilon_\omega = \frac{\varepsilon_0}{1 + \frac{\omega^2}{\omega_0^2} + (-i\omega\tau_0)^\gamma} \]  

(4.6)

with a change in notation: \( \Delta\theta \rightarrow \varepsilon_\omega \) and \( \Delta\theta_0 \rightarrow \varepsilon_0 \), where \( \varepsilon_0, \omega_0, \tau_0 \) and \( \gamma \) are current and position dependent. The resonance term corresponds to the delay, with \( \tau_{\text{delay}} \approx 1/\omega_0 \) for values of \( \gamma \approx 1 \). The current dependence of the fitting parameters, for both free and pinned contacts, at three positions are shown in Fig.(4.4). The position dependence of the relaxation and delay times are shown in Fig.(4.5).

Note (Fig.(4.3)) that the fits are much better away from the contacts than at \( x = 0 \), where the absence of delays (i.e. \( \omega_0 = \infty \)) essentially reduces the number of parameters. The comparatively poor fits at \( x = 0 \) reflect the enhancement of the in-phase response with respect to the quadrature compared to perfect relaxation; Eq.(4.6) attempts to accommodate this enhancement by reducing \( \gamma \) (for small currents) and decreasing \( \tau_0 \) by \( \approx 20\% \) (at all currents) with respect to \( 1/\omega_{\text{peak}} \). Away from the contacts, the expression fits the data very well, except at the highest currents, where it underestimates the magnitude of the inverted in-phase strain at high frequencies.

In general, the relaxation time decreases rapidly with increasing current (Fig.(4.4a)), as we also observed in K\(_{0.3}\)MoO\(_3\) [103, 104]. The inset to the figure shows the behavior near threshold; as the phase-slip rate vanishes, \( \tau_0 \) saturates at the diffusion time \( (L^2/(\pi^2 D)) \) for pinned contacts. The apparent position dependence of \( \tau_0 \) for low currents is an artifact of the relatively poor fits here. However, for free contacts, \( \tau_0 \) actually has a maximum at \( \approx 1.3 j_T \) (i.e. the frequency of the peak in the quadrature response has a minimum); this is another unexpected consequence of outside phase-slip slowing the dynamic response.

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Figure 4.4: Current dependence of the fitting parameters to Eq.(4.6) for \( x = 0 \) (up triangles), \( x = 100 \mu m \) (circles), and \( x = 200 \mu m \) (down triangles). Solid symbols (dashed curves) correspond to pinned contacts and open symbols (solid curves) correspond to free contacts, all with \( E_p = \text{constant} \). (The curves are guides to the eye.) Note that at \( x = 0 \), \( 1/\omega_0 = 0 \) (not shown). The inset to (a) shows the dependence of \( \tau_0 \) on small currents in a linear scale.

between the contacts. That saturation of \( \tau_0 \) was observed in our electro-optic experiments on \( \text{K}_0.3\text{MoO}_3 \) (see chapter 5 and [104]) is therefore an indication that we had pinned contacts, as expected.

Away from the contacts, the delay times decrease with increasing current (Fig.(4.4b)), but more slowly than the relaxation times, so that at the highest currents the response actually becomes underdamped (\( \omega_0\tau_0 < 2 \)). Both time constants increase with distance from the contact (Fig.(4.5)). All these features were also experimentally observed in \( \text{K}_0.3\text{MoO}_3 \) [103]. For small currents, the delay time varies linearly with \( x \); in \( \text{K}_0.3\text{MoO}_3 \), we interpreted this as a flow of strain from the contact with constant velocity [103] mentioned above. However, this linear dependence does not hold at higher currents, as seen in Fig.(4.5b).

Also, as we experimentally observed in \( \text{K}_0.3\text{MoO}_3 \), the amplitude of the response continues growing with current in the phase-slip region, as required for current conversion, but saturates (for \( j > 2j_T \)) in the "linear" region, where the strain can be viewed as a finite-size effect [51] (see section 1.4). However, in the simulation \( \gamma \approx 1 \) even for small currents (away from the contacts), whereas for \( \text{K}_0.3\text{MoO}_3 \) we generally observed \( \gamma \) to greatly decrease at low currents [103], which we interpreted in terms of a broadening distribution of relaxation times.

The time dependence of the voltage \( V(t) \) across the sample, calculated from Eq.(4.1)
Figure 4.5: Position dependence of (a) average relaxation time and (b) delay time for a few currents. Solid symbols (dashed curves) correspond to pinned contacts and open symbols (solid curves) correspond to free contacts, all with $E_p = \text{constant}$. (The curves are guides to the eye.)
as discussed in B, for a current density $j_{total} = 3j_T$ and frequencies 3.0 and 12.5 kHz, is shown in Fig.(4.6) for the two cases considered with $E_p = \text{constant}$: pinned contacts and free contacts. Note that at both frequencies the voltage is larger for the case of pinned contacts, which is consistent with the results shown in Fig.(4.2) where the strain is larger for the case of pinned contacts. For low frequencies, the peaks at that times correspond to the well known "overshoot" effect discovered by Gill [105] and are due to repolarization current. For squares wave periods close to or less than this overshoot time, the voltage response becomes very distorted.

As stated above, these simulation results have several qualitative similarities with our electro-optic results on blue bronze [103]: in particular, the current and position dependencies of the amplitude, relaxation time, and delay time. Note that both time constants in blue bronze are one to two orders of magnitude slower (at $T \sim 80$ K) than for the simulated results [103]. This is reflected in the different diffusion constants of semiconducting K$_{0.3}$MoO$_3$ and semimetallic NbSe$_3$ (Eq.(4.5)): while blue bronzes CDW elastic constant is an order of magnitude larger than that of NbSe$_3$ [104], its single particle resistivity is $\sim 300$ times larger (so that $\rho_c \gg \rho_e$ for blue bronze) [10]. There are important factors which prevent quantitative modeling of our blue bronze results, however:

a) The K$_{0.3}$MoO$_3$ experiments were voltage driven [45,103,104], whereas the simulations are current driven. This distinction is not trivial, because the electric field is not constant in the sample and in fact varies with time as well as position, so that a square-wave current does not correspond to a square-wave voltage, as shown in Fig.(4.6). This factor prevents quantitative comparisons of measured and simulated current dependences, especially at high frequencies and small currents [6,9].
b) Strains in the CDW are screened by quasiparticles, so that the single particle density, \( n_s \), will change, with \( \Delta n_s \approx -Q\varepsilon/\pi A \), where \( A \) is the area/conducting chain, see section 1.4.1. In \( K_{0.3}\text{MoO}_3 \), \( n_s \) is much smaller than in \( \text{NbSe}_3 \), so that \( \Delta n_s/n_s \) may not be negligible (Although our electro-optic measurements only give relative values of the strain, the magnitude of the strain expected from Eq.(4.1) is comparable to that of \( \text{NbSe}_3 \)), with the consequence that the single particle resistivity cannot be treated as a constant in Eq.(4.1) [55]. However, the CDW elasticity is also approximately inversely proportional to \( n_s \) [106], making the diffusion constant (Eq.(4.5)) roughly independent of \( n_s \). Our observation that the strains in blue bronze do not pile up on one side of the sample but stay approximately antisymmetric about the center [96, 103] therefore suggests that the phase slip rate is independent and pinning field inversely proportional to \( n_s \). However, the pinning field was observed to increase with optical excitation of quasiparticles in both \( K_{0.3}\text{MoO}_3 \) and \( \text{TaS}_3 \) at low temperatures [107, 108]. If this is also true at the higher temperatures where we did our electro-optic measurements, it would suggest that the parameters of Eq.(4.1) should be replaced with their average (i.e. non-local) values.

c) Equation (1.10) was found to be a good fit to the phase-slip rate by the Cornell group for their \( \text{NbSe}_3 \) sample for strains near the contact, but did not fit \( r_{ps} \) away from the contact, see Fig.(1.8) (where the rate of phase-slip is very small and doesn’t effect the strain profile significantly). There have been no direct experimental probes of phase-slip in \( K_{0.3}\text{MoO}_3 \), however, so it is not clear if a similar expression is valid and, if so, what value of \( \varepsilon_B \) is appropriate.

d) In \( K_{0.3}\text{MoO}_3 \), we occasionally observed a decay of the electro-optic signal at long times as discussed in section 3.3.1, but were unable to determine how this decay varied with position or voltage. Such decay is not a feature of Eq.(4.1). It is presumably not a consequence of the electro-optic experiments being voltage-driven, rather than current-driven, since this difference is expected to be most pronounced at short-times and high frequencies. We suggest that the decay of the electro-optic response may be a consequence of \( E_p \) and \( r_{ps}(\varepsilon) \) varying with position, not only the distance from contact but also across the sample cross-section (e.g., enhanced pinning near the surface).
CHAPTER 5: SEARCH FOR CRITICAL BEHAVIOR AT CDW DEPINING

5.1 Introduction

As was discussed in section 1.2, for low applied forces, the CDW is pinned to the lattice by impurities, but at large voltages it can break free and carry collective current. One of the central questions has been the extent to which the onset of CDW sliding, at applied threshold voltage $V_{on}$, can be considered a dynamic critical transition of an elastic medium, as first proposed by Fisher [94,109]. From renormalization group (RG) calculations, the CDW drift velocity is expected to vary as $v_{CDW} \sim [V/V_{on} - 1]^\zeta$, with critical exponent $\zeta \sim 5/6$ (in three dimensions) [110], but experimental attempts to measure the critical exponent of CDW velocity (i.e., current) have yielded a variety of values for $\zeta$ [102], possibly reflecting effects of imperfect electrical contacts on the CDW velocity. Indeed, the electric field and CDW current are nonuniform, increasing and decreasing, respectively, near (typically ~ 100 μm) current contacts where single-particle current must convert to collective current [6,9,51] so that interpreting $I-V$ measurement is complicated even for nonperturbative contacts [102]. Furthermore, there have been no estimates of the width of the critical region for sliding CDWs; below threshold, the critical region has been theoretically estimated [111] to be $|V/V_{on} - 1| < 0.1$, but, as discussed there, there is no obvious relationship between critical behavior above and below $V_{on}$. In addition to the CDW velocity, other properties are expected to have critical behavior. The RG calculations [110] have shown that the dynamic phase (i.e., velocity) correlation length diverges as $\xi \sim |V/V_{on} - 1|^{-\nu}$, with $\nu \sim 1/2$ (different from the exponent for the static correlation length below threshold) [111], while changes in the CDW phase diffuse with weakly divergent diffusion constant $D \sim |V/V_{on} - 1|^{-2\nu + \zeta}$. However, we knew of no experimental measurements of the critical properties of $D$ or $\zeta$.

Motivated by these facts, the main objective in this chapter is to attempt to observe a critical behavior in the diffusion constant or another quantity related to as polarization the relaxation time, using electro-transmittance measurements.

5.2 Model

When a voltage above threshold is applied to a CDW conductor, the CDW compresses on one side of the sample and rarefies on the other, resulting in a spatially dependent CDW phase, $\phi$ (or equivalently, shift in CDW wave vector $\Delta Q = \frac{\partial \phi}{\partial x}$) as discussed in section 1.4. In chapter 4 we modeled the behavior of the CDW polarization dynamics in the frequency domain using a phenomenological model given by Eq.(4.1) and that we rewrite as

$$\frac{\partial \varphi}{\partial t} \approx \beta (I - \frac{V_{on}}{R_0}) + D \frac{\partial^2 \varphi}{\partial x^2} - \int_{-\infty}^{x} r_{ps}(x')dx'$$

(5.1)
where $I$ is the total current in the sample, $R_0$ is the Ohmic resistance below threshold, $\beta$ is a constant, $D \propto K$ is the diffusion constant ($K$ is the CDW elastic constant) given by Eq.(4.5) for noncritical voltages, and the slip rate $r_{ps}$, is a strongly nonlinear function of strain, see Eq.(1.10). Phase slip constitutes an irreversible, i.e., "plastic", change in the local phase required for current conversion [6, 9]. Because of the phase-slip term, the response time $\tau$ for phase changes decreases rapidly with increasing current, as discussed in section 4.3.3, but for voltages near threshold, $r_{ps}$ will be very small, so that $\tau$ is given by (see A, Eq.(A-19))

$$\tau(V) = \frac{L^2}{\pi^2 D(V)} \quad (5.2)$$

where $L$ is the sample length and $D$ is expected to be constant except in the critical region. We have taken $n = 1$ as the main relaxation time as discussed in section 4.3. Then one would expect the time constant to actually slowly decrease in the critical region as $D$ diverges:

$$\tau \sim |V/V_{on} - 1|^{2\nu-\zeta} \sim |V/V_{on} - 1|^{1/6} \quad (5.3)$$

Indeed, the RG calculations of Refs. [94, 109] and [110] assume that this "elastic" i.e., negligible phase-slip condition, holds in the critical regime near threshold. Alternatively, it has been suggested that significant amounts of phase slip occur at all voltages and throughout the sample, so that depinning becomes a rounded first order transition [112], and some experiments do suggest that phase slip is pervasive [113]. However, the measured spatial profiles of CDW strain [6, 9, 45, 51] certainly indicate that phase slip concentrates at the contacts and grows rapidly with voltage above threshold. While our present results will be discussed assuming that phase slip vanishes at threshold, the validity of this assumption remains an open question.

### 5.3 In search of Critical behavior

We have attempted to observe critical behavior in the electro-optic relaxation time, and hence diffusion constant, by extending our previous frequency dependent measurements in $K_{0.3}\text{MoO}_3$ closer to threshold: $V < 1.1V_{on}$.

#### 5.3.1 Experimental procedure

The experimental technique is similar to that used in section 2.2. A $K_{0.3}\text{MoO}_3$ crystal cleaved to a thickness between 5 and 10 $\mu$m, was chosen to have similar voltage and frequency dependence of its electrotransmittance and electroreflectance, showing that the CDW strains were fairly uniform in the sample cross section, well-defined onset voltages, well-defined relaxation peaks, i.e., relatively large values of $\gamma$ and negligible delays near the contacts and low-frequency decays at low voltages. Gold films were evaporated on the
ends of the crystal to serve as current contacts. The resulting sample length and width were 650 and 120 μm. A symmetric, bipolar square-wave voltage, 1.5 Hz < ω/2π < 2 kHz, was applied to the sample, periodically reversing the CDW strain, and the resulting relative change in reflectance or transmittance measured. All measurements were made at relatively high temperatures where the CDW is believed to be weakly i.e., collectively pinned [102] and the critical models [94,109,110] are relevant, with the light spot adjacent to a current contact to minimize the resonance term in Eq.(3.1), as discussed below.

5.3.2 Results and Discussion

Figure 5.1 shows the voltage dependence of the electroreflectance, both in phase and in quadrature with a ω/2π = 25 Hz square wave at T = 78 K. Also shown is the voltage dependence of the dc resistance of the sample. Note that the electro-optic onset voltage (determined with a precision of 0.3 mV), where the CDW becomes depinned, is considerably below the threshold for nonlinear current, V_T (Refs. [45] and [68]), suggesting a broad voltage region where phase-slip rate is low, as discussed below.

Figure 5.2 shows the frequency dependence of the electroreflectance at T = 78 K at a few voltages. Note that at the higher voltages the in-phase response becomes inverted at high frequency, corresponding to the resonance term in Eq.(3.1), but that this inversion is negligible at the lower voltages, so these fits are not sensitive to ω_0 i.e., ω_0 > 1 kHz. Therefore, for internal consistency, fits were made to Eq.(3.1) omitting the resonance term at all voltages; the fitting curves are shown in the figure. While these do a poor job at the higher frequencies for the higher voltage curves, including the resonance term mostly has the effect of decreasing the value of the exponent and has no significant effect on τ_0.
Indeed, the fitted values of $1/\tau_0$, shown by the vertical arrows in Fig.(5.2), agree closely with $\omega_{\text{peak}}$, the peak frequency of the quadrature response. This is true even for $\gamma \sim 0.7$, our smallest value see Fig.(5.3b), where the resulting distribution of relaxation times is a decade wide [92]. Hence our values of $\tau_0$ are largely independent of the fitting function. Figure 5.3 shows the dependence of the fitting parameters on voltage, normalized to $V_{\text{on}}$

![Graph](image)

Figure 5.2: Frequency dependence of the electroreflectance at $T = 78$ K. The in-phase and quadrature responses at a few voltages are shown. The curves show the fits to Eq.(3.1) with the resonance terms omitted (i.e., $\omega_0 = \infty$); the values for $\gamma$ for each fit are given. The vertical arrows show the values of $1/2\pi\tau_0$ of the fits.

and plotted on a linear scale, at a few temperatures. Except at $T = 78$ K, the relaxation time Fig.(5.3a) is still increasing at the lowest voltage at which, because of the rapidly decreasing amplitude of the response near $V_{\text{on}}$ [Fig.(5.3c)], we could determine it. Note that the maximum value of the time constant is $\tau_0(\text{max}) \approx 20$ ms so that $1/2\pi\tau_0(\text{max}) \sim 8$ Hz
is within our measured frequency window and we are not instrumentally limited. Also note that the voltage dependence of \( \tau_0 \) is considerably stronger than for the samples previously measured in chapter 3; this sample dependence of CDW strain properties is presumably a manifestation of different contact qualities as well as distributions of pinning impurities and other defects [45,103].

Figure 5.3: Voltage dependence of the fitting parameters [a) \( \tau_0 \), b) \( \gamma \) and c) \( A_0 \)] at the temperatures indicated. In a), the fitting uncertainties for \( \tau_0 \) are indicated, the horizontal bar shows the uncertainty in \( V/V_{on} \) at low voltage, and the vertical arrows show the values of \( V_T/V_{on} \) at each temperature.

As mentioned above, the decrease in \( \tau_0 \) with increasing current at "high voltages" reflects the increasing rate of phase slip. It is surprising that this behavior continues to voltages below \( V_T \), the threshold of measurable nonlinear current (shown by vertical arrows in the figure). That is, the polarization dynamics are still dominated by plastic phase slip at voltages as low as \( V \sim 1.06V_{on} \). While the resulting strong voltage dependence of \( \tau_0 \) could mask any weak divergence of \( D \), the fact that phase slip dominates indicates that we are not yet in the elastic, critical regime considered in Ref. [110]. At \( T = 78 \) K, on the other hand, the relaxation time saturates at low voltage (also apparent in Fig.(5.2), so here we are presumably in the elastic and diffusive limit. This is consistent with the fact that here \( V_T/V_{on} \sim 1.4 \), while \( V_T/V_{on} \sim 1.2 \) at the other temperatures, indicating a larger voltage
region in which the rate of phase slip is very low at 78 K than elsewhere. However, even at 78 K there is no indication of a critical decrease in relaxation time at the lowest voltages, again giving \(|V/V_{on} - 1|_{critical} < 0.06\) as an upper limit of the critical voltage region; this is the essential result of this work.

We can also use Eq.(5.2) with the saturation value of the relaxation time, \((\tau_0)_{sat} \sim 20\) ms to estimate the noncritical value of the diffusion constant\(^1\): \(D(\infty) \sim 0.02\ cm^2/s.\) Then using Eq.(4.5)

\[
D(\infty) = \left( \frac{Q}{cm} \right)^2 \frac{K}{(\rho_0 + \rho_c)}
\]

(5.4)

where \(\rho_0\) and \(\rho_c\) are the single-particle and high-field CDW resistivities, with \(\rho_c \ll \rho_0\) \((\sim 0.6\Omega\ cm\ at\ 80\ K)\) [10, 97] in semiconducting \(K_{0.3}MoO_3\), \(n \sim 5 \times 10^{21}\ cm^{-3}\) is the condensate density [10] \(Q \sim 0.7\ \AA^{-1}\) [18,97] and \(K\) is the CDW elastic constant, we find that \(K \sim 0.1\ eV/\AA.\) This value is an order of magnitude larger than that estimated for NbSe\(_3\), [5,9] which is appropriate since \(K\) is expected to increase with decreasing temperature in semiconducting \(K_{0.3}MoO_3\) as the density of screening quasiparticles falls, whereas NbSe\(_3\) remains metallic in the CDW state [1]. This increased stiffening in \(K_{0.3}MoO_3\) has also been observed as a large increase in phason velocity, \(v_\phi,\) above its mean-field value at low temperatures [18], see Fig.(5.4). In fact, our value of \(K\) is consistent with that expected from the \((T = 80\ K)\) value of \(v_\phi \sim 1.4 \sim 10^6\ cm/s;\) [18] i.e.,

\[
K = \left( \frac{2Q}{\pi} \right) m_F v_\phi^2
\]

(5.5)

where the factor in parentheses is the linear density of CDW electrons (two bands condense into the CDW state giving 4 electrons/wavelength) [10,110,114] and the effective "Fröhlich" mass [1] has been estimated as \(m_F \sim (150 - 350) m_e\) [18].

Alternatively, one might have suspected that as phase slip becomes negligible near threshold, diffusion does not occur across the whole sample length but becomes limited to the correlation length. Then instead of Eq.(5.2), one would have \(\tau \approx \xi^2/D,\) and the relaxation time would critically diverge with exponent \(\zeta = 5/6\) [110]. While our \(T \neq 78\ K\) data are not inconsistent with such critical slowing down, we have presumably not reached the elastic limit appropriate to the RG calculations [110] at these temperatures. On the other hand, the \(T = 78\ K\) saturated value of \((\tau_0)_{sat} \sim 20\ ms,\) which we do associate with elastic behavior, seems too long to be due to diffusion across a noncritical value of \(\xi.\) Attempts to measure the correlation length in \(K_{0.3}MoO_3\) with x-ray diffraction have been resolution limited so it is only known that \(\xi > 1.6\ \mu m\) [115] but it is unlikely that the noncritical correlation length is large enough (e.g., > 100 \(\mu m\)) to give a physical value for \(K\) from Eq.(5.4). In principal, a straightforward test of \((\tau_0)_{sat} = L^2/\pi^2 D(\infty)\) would be to

\(^1\)For applied square waves, the solution of Eq.(5.1) in the diffusive limit has an average relaxation time only a few percent larger than the "free decay" value of Eq.(5.2). See section 4.3 for further details.
Figure 5.4: Thermal evolution of the phase mode velocity in the $b^*$ direction neglecting (□) and accounting for (●) the anisotropy of the dispersion surface. The solid line is calculated from the expression [18]: $v_{b^*} = v_F \left( \frac{m_e}{m^*} \right)^{1/2} \left( 1 + \frac{\exp(\Delta/T)}{(2\pi \Delta/T)^{1/2}} \right)^{1/2}$, where $\Delta$ is the temperature dependent half Peierls gap, $v_F$ is the Fermi velocity and $m_e/m^*$ is the CDW reduced mass [19]. In this relation, effects of screening of the long Coulomb force are involved compare saturated time constants for samples of different lengths. However, for low voltages, the elastic strain (and hence electro-optic response) $\sim 1/L$ [51], so working with much longer samples is not feasible. Working with much shorter samples would require preparing electrical contacts to ensure uniform current flow as well as improving our $\sim 50 \mu m$ spatial resolution.
CHAPTER 6: CONCLUSIONS

We used infrared electrotransmittance to probe the dynamics of CDW repolarization. Long (millisecond) relaxation and delay times even for voltages well above the depinning threshold suggest that the response involves the motion of macroscopic objects, presumably CDW phase dislocation lines [51]. This appears to be true for the contact strains driving phase slip as well as the bulk polarization. Most striking is the growth in the delay time with position away from the contacts. The temperature dependence of the time constants suggests that quasiparticles influence the dynamics of polarization only through their effect on the CDW current.

Furthermore, we extended the phase-slip model of Reference [9] to study the dependence of CDW strain on the frequency and amplitude of applied square-wave currents. We have found that pinning the phase at the current contacts increases the rate of change of strain everywhere, as compared to allowing the phase to slip outside the contacts. Adjacent to the contacts, the phase change is essentially relaxational, but a delay develops away from the contacts. Both the relaxation time and delay time increase with increasing distance from a contact and both decrease with increasing current, with the result that the response of the phase becomes underdamped at high currents. All of these effects were observed in our electro-optic measurements on K$_{0.3}$MoO$_3$ [103].

Finally, we also used the electro-optic technique to measure the CDW phase relaxation time as functions of voltage with voltages as small as 1.06$V_{on}$. At most temperatures, the relaxation time is still increasing at the lowest voltages, indicating that the sample is still in the plastic (and presumably noncritical) limit. However, at one temperature we observe the relaxation time to saturate, with no indication of critical "speeding up" (i.e., divergence of the diffusion constant), giving an upper limit to the critical region of $|V/V_{on} - 1|_{critical} < 0.06$. The saturated relaxation time allowed us to estimate the noncritical value of the CDW diffusion constant as $D(\infty) \sim 0.02 \text{ cm}^2/\text{s}$, consistent with the value expected from the measured phason dispersion [18].
Appendices
A Solution of the equation that describes the CDW dynamics with $E_p = \text{constant}$ and $r_{ps} = 0$

The general solution of the diffusion equation

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} + \Psi(x, t) \quad (A-1)$$

(assuming $D = \text{constant}$) in the domain $0 \leq x \leq L$ and conditions

$$\phi = f(x) \quad \text{at} \quad t = 0 \quad (\text{Initial condition}) \quad (A-2a)$$

$$\phi = g_1(t) \quad \text{at} \quad x = 0 \quad (\text{boundary condition}) \quad (A-2b)$$

$$\phi = g_2(t) \quad \text{at} \quad x = L \quad (\text{boundary condition}) \quad (A-2c)$$

is given by [116]

$$\phi(x, t) = \int_0^L f(\zeta) G(x, \zeta, t) d\zeta + \int_0^t \int_0^L \Psi(\zeta, \tau) G(x, \zeta, t-\tau) d\zeta d\tau$$

$$+ D \int_0^L g_1(\tau) H_1(x, t-\tau) d\tau - D \int_0^L g_2(\tau) H_2(x, t-\tau) d\tau \quad (A-3)$$

where

$$G(x, \zeta, t) = \frac{2}{L} \sum_{n=1}^{\infty} \sin \left( \frac{n\pi}{L} x \right) \sin \left( \frac{n\pi}{L} \zeta \right) \exp \left( -\frac{Dn^2 \pi^2 t}{L^2} \right) \quad (A-4)$$

and

$$H_1(x, t) = \frac{\partial}{\partial \zeta} G(x, \zeta, t)_{\zeta=0} \quad H_2(x, t) = \frac{\partial}{\partial \zeta} G(x, \zeta, t)_{\zeta=L} \quad (A-5)$$

In the particular case when $\Psi(x, t) = F = \text{constant}$ and $g_1(t) = g_2(t) = 0$, the solution given by Eq.(A-3) reduces to

$$\phi_1(x, t) = \frac{4F \tau_0}{\pi} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi}{L} x \right) \left[ 1 - \exp \left( -n^2 \frac{t}{\tau_0} \right) \right] \quad (A-6)$$

where

$$\tau_0 = \frac{L^2}{D\pi^2} \quad (A-7)$$

The steady solution is obtained when $t \rightarrow \infty$
Figure 1: Position dependence of (a) phase and (b) strain for the case of pinned contacts at \( x = 0 \) and \( x = L \), \( E_p \) = constant and no phase slip.

\[
\phi_{1s}(x, \infty) = \frac{4F \tau_0}{\pi} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi x}{L} \right)
\]  

(A-8)

Furthermore, Eq.(A-8) is the Fourier series of the 2L-period odd function

\[
\phi_{1s'}(x, \infty) = \begin{cases} 
-\frac{F}{2D} \left( x - \frac{L}{2} \right)^2 + \frac{F L^2}{8D} & 0 \leq x \leq L \\
\frac{F}{2D} \left( x + \frac{L}{2} \right)^2 - \frac{F L^2}{8D} & -L \leq x \leq 0
\end{cases}
\]

(A-9)

which corresponds to a concave downward parabola shifted to the right by \( L/2 \).

Now, let us use this result to find the solution of the equation Eq.(4.1) without the phase-slip term \( r_{ps} \) and assuming that the pinning field \( E_p \) is constant

\[
\frac{\partial \phi}{\partial t} = \frac{Q}{e n_c} \frac{1}{\rho_c + \rho_s} \left[ \rho_s \cdot j_{\text{total}} - E_p + \frac{Q}{e n_c} K \frac{\partial^2 \phi}{\partial x^2} \right]
\]

(A-10)

The previous equation is identical to Eq.(C-1) if we match \( F = \frac{Q}{e n_c} \frac{1}{\rho_c + \rho_s} [\rho_s \cdot j_{\text{total}} - E_p] \) and \( D = \left( \frac{Q}{e n_c} \right)^2 \frac{K}{\rho_c + \rho_s} \). Thus, while the driving force \( F \) is given in terms of the total current density, the diffusion constant \( D \) is proportional to the CDW elastic constant. This solution is valid for \( \rho_s \cdot j_{\text{total}} - E_p > 0 \), i.e., for a sliding CDW. If the current were reversed then this condition would become \( -\rho_s \cdot j_{\text{total}} + E_p < 0 \). Hence, the condition for sliding CDW is imposed by \( |\rho_s \cdot j_{\text{total}} - E_p| > 0 \). Notice that the strain \( \varepsilon = \frac{1}{Q} \frac{\partial \phi}{\partial x} \) in the steady state \((t \to \infty)\) is given by

\[
\varepsilon(x) = \frac{1}{Q} \frac{\partial \phi}{\partial x} = -\frac{F}{Q \cdot D} \left( x - \frac{L}{2} \right) \quad 0 \leq x \leq L
\]

(A-11)

Thus, as a consequence of the polarization the CDW becomes strained and the maximum and minimum strain occurs at the current contacts \( x = 0 \) and \( x = L \) respectively as can be seen in the Fig.1
Now let us apply alternating symmetric bipolar pulses of period \( T = \frac{2\pi}{\omega_0} = 2t^* \). The response right after reversing the driving force \((-F)\) is given by Eq.(A-3) (first negative pulse)

\[
\phi_2(x, t) = \int_0^L \phi_1(\zeta)G(x, \zeta, t)d\zeta - F \int_0^L \int_0^t G(x, \zeta, t - \tau)d\zeta d\tau
\]

\[
= \frac{4F\tau_0}{\pi} \sum_{n=odd}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi}{L}x \right) \left[ 2 \exp\left( -\frac{n^2t^*}{\tau_0} \right) - \exp\left( -\frac{n^2(t^* + t)}{\tau_0} \right) - 1 \right]
\]

To evaluate these integrals, I made use of the results*1

Similarly, it can be shown that the time and position dependence of the phase after \( p \) and \( p + 1 \) reversals are

\[
\phi_p(x, t) = \frac{4F\tau_0}{\pi} \sum_{n=odd}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi}{L}x \right) \left[ 1 - 2e^{-n^2\frac{t}{\tau_0}} \left( \frac{1}{2} e^{-(p-1)n^2\frac{t^*}{\tau_0}} + \sum_{k=0}^{k=p-2} (-1)^k e^{-kn^2\frac{t^*}{\tau_0}} \right) \right]
\]

\[
\phi_{p+1}(x, t) = \frac{4F\tau_0}{\pi} \sum_{n=odd}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi}{L}x \right) \left[ -1 + 2e^{-n^2\frac{L}{\tau_0}} \left( \frac{1}{2} e^{-pn^2\frac{t^*}{\tau_0}} + \sum_{k=0}^{k=p-2} (-1)^k e^{-kn^2\frac{t^*}{\tau_0}} \right) \right]
\]

Notice that the first term in the curly parenthesis is negligible when \( p > \frac{\tau_0}{n^2\tau^*} = \frac{L^2\omega}{D\pi\pi\tau^*} \), implying that the response becomes periodic more rapidly for low frequencies and large diffusion constant as expected. Thus, after a sufficient number of consecutive pulses of opposite polarity, the two previous expressions reduce to

\[
\phi_+(x, t) = \frac{4F\tau_0}{\pi} \sum_{n=odd}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi}{L}x \right) \left[ 1 - 2\frac{e^{-n^2\frac{L}{\tau_0}}}{1 + e^{-n^2\frac{L}{\tau_0}}} \right] \tag{A-12}
\]

\[
\phi_-(x, t) = \frac{4F\tau_0}{\pi} \sum_{n=odd}^{\infty} \frac{1}{n^3} \sin \left( \frac{n\pi}{L}x \right) \left[ -1 + 2\frac{e^{-n^2\frac{L}{\tau_0}}}{1 + e^{-n^2\frac{L}{\tau_0}}} \right] \tag{A-13}
\]

the subscripts + and − represent the polarities of the current. From the definition of strain \( \varepsilon = \frac{1}{Q} \frac{d\phi}{dx} \) we have

\[
\varepsilon_+(x, t) = \frac{4F\tau_0}{QL} \sum_{n=odd}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L}x \right) \left[ 1 - 2\frac{e^{-n^2\frac{L}{\tau_0}}}{1 + e^{-n^2\frac{L}{\tau_0}}} \right] \tag{A-14}
\]

\[
\int_0^L \sin \left( \frac{n\pi}{L} \zeta \right) \sin \left( \frac{m\pi}{L} \zeta \right) d\zeta = \frac{L}{2} \delta_{mn}
\]

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\[ \varepsilon_\omega(x, t) = \frac{4F\tau_0}{QL} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L} x \right) \left[ -1 + 2 \frac{e^{-n^2 t/\tau_0}}{1 + e^{-n^2 t/\tau_0}} \right] \tag{A-15} \]

The time dependence of the strain \( \varepsilon(x, t) \) can be written as

\[
f(t) = \begin{cases} 
-1 + 2Ae^{-bt} & 0 \leq t \leq t^* \\
1 - 2Ae^{-b(t-t^*)} & t^* \leq t \leq 2t^* 
\end{cases}
\tag{A-16}
\]

where \( A = \frac{1}{1+e^{-n^2 \tau_0}} \) and \( b = -n^2/\tau_0 \). The first harmonic Fourier coefficients of \( f(t) \) with period \( T = 2t^* = \frac{2\pi}{\omega_0} \) are

\[
a_1 = \frac{1}{T} \int_0^{2t^*} f(t) \cos (\omega_0 t) \, dt = \frac{\omega_0 \tau_0}{n^2} \frac{\omega_0 \tau_0}{1 + (\omega \tau_n)^2} \]

\[
b_1 = \frac{1}{T} \int_0^{2t^*} f(t) \sin (\omega_0 t) \, dt = \frac{2}{\pi} \frac{1}{1 + (\omega \tau_n)^2} \]

To evaluate these integrals have made use of the results\(^2\)

Hence, the first component Fourier of the in-phase and quadrature of the strain are given by: (we have renamed the frequency \( \omega_0 \) as \( \omega \))

\[
(\varepsilon_\omega)\text{In-Phase} = \frac{8F\tau_0}{QL\pi} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L} x \right) \times \frac{1}{1 + (\omega \tau_n)^2} \tag{A-17}
\]

\[
(\varepsilon_\omega)\text{Quadrature} = -\frac{8F\tau_0}{QL\pi} \sum_{n=\text{odd}}^{\infty} \frac{1}{n^2} \cos \left( \frac{n\pi}{L} x \right) \times \frac{\omega \tau_n}{1 + (\omega \tau_n)^2} \tag{A-18}
\]

where

\[
\tau_n = \frac{\tau_0}{n^2} = \frac{L^2}{\pi^2 n^2 D} \tag{A-19}
\]

---

\(^2\) \( \int e^{bx} \sin ax \, dx = \frac{1}{a^2 + b^2} \exp(bx)(b \sin ax - a \cos ax) \) and \( \int e^{bx} \cos ax \, dx = \frac{1}{a^2 + b^2} \exp(bx)(a \sin ax + b \cos ax) \)
B Potential difference between the current contacts

Using the definition given by Eq.(1.28), Eq.(4.1) can be rewritten as

\[
\frac{\partial \phi(x,t)}{\partial t} + \int_{-\infty}^{x} \tau_{ps}(x',t)dx' = \frac{Q}{Aen_c \rho_c + \rho_s} \frac{1}{\rho_s i_{\text{total}} - E_p(i_c) + \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2}}
\]

or

\[
\frac{\partial \phi(x,t)}{\partial t} = \frac{Q}{Aen_c \rho_c + \rho_s} \left[ \rho_s i_{\text{total}} - E_p(i_c) + \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2} \right]
\]

(B-1)

using the relations \( \epsilon = \frac{1}{Q} \frac{\partial \phi}{\partial x} \), \( i_c = A \frac{en_c}{Q} \frac{\partial \phi}{\partial x} \), \( i_{\text{total}} = i_s + i_c \), \( E = \rho_s i_s \) the previous equation becomes

\[
\rho_s i_{\text{total}} - E_p(i_c) = \frac{\partial \phi(x,t)}{\partial t} \left( A \frac{en_c}{Q} \right) (\rho_c + \rho_s) - \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2}
\]

\[
= (\rho_c + \rho_s) i_c - \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2}
\]

\[
\rho_s (i_c + i_s) - E_p(i_c) = (\rho_c + \rho_s) i_c - \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2}
\]

\[
E - E_p(i_c) = \rho_c \cdot i_c - \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2}
\]

(B-2)

The potential difference \( V(t) \) between the current contacts can be obtained by numerically integrating Eq.(B-2) respect to position between \( x = 0 \) (left contact) and \( x = L \) (right contact). Thus \( V = -\int E \cdot dx \) yields

\[
V(t) = \int_0^L \left( \frac{Q}{en_c} K \frac{\partial^2 \phi}{\partial x^2} - \rho_c \cdot i_c - E_p(i_c) \right) dx
\]

(B-3)
C Solution method that describes the CDW dynamics with \( r_{ps} \neq 0 \)

In this appendix we discuss briefly the numerical solution of the equation Eq.(4.1) using the Finite Difference Method. The specific initial-boundary-value-problem we wish to solve is the following:

\[
\frac{\partial \varphi}{\partial t} = F + D \frac{\partial^2 \varphi}{\partial x^2} + \int_{-\infty}^{x} r_{ps}(x')dx'
\]  

where \( F = \frac{Q}{e_{c} \rho_{c} + \rho_{s}} [\rho_{s} \cdot f_{\text{total}} - E_{p}] \), \( D = \left( \frac{Q}{e_{c}} \right)^{2} \frac{K}{\rho_{c} + \rho_{s}} \) and \( r_{ps} \) is the phase-slip rate given by Eq.(1.10). The range of \( x \) is defined by \( 0 \leq x \leq L \).

We discretize the domain into a finite number of points where we intend to compute the solution of Eq.(C-1). For convenience, we will use a uniform grid, with a grid spacing \( \Delta x = L/M \). We will refer to one of the points in the grid as \( x_k = k \Delta x \), where \( k = 0, ..., M \). Likewise we discretize the time interval into \( N \) times, separated by a time increment \( \Delta t \), and only compute the solution for times \( t_n = n \Delta t \), \( n = 0, ..., N \). Our aim is to compute the solution of Eq.(C-1) for all values \( \varphi_k^n = \varphi(k \Delta x, n \Delta t) \).

We now have a grid that approximates the domain \( x \in [0, L], t \geq 0 \). The next step it to define approximations to the partial derivatives appearing in Eq.(C-1). We use the forward approximation for temporal derivatives and the centered approximation for spatial derivatives [117]:

\[
\frac{\partial \varphi}{\partial t} \approx \frac{\varphi_{k}^{n+1} - \varphi_{k}^{n}}{2 \Delta t}
\]  

\[
\frac{\partial^2 \varphi}{\partial x^2} \approx \frac{\varphi_{k+1}^{n} - 2 \varphi_{k}^{n} + \varphi_{k-1}^{n}}{(\Delta x)^2}
\]  

Substituting the expression for the temporal derivative (Eq.(C-3)) and the expression for the second-order spatial derivative (Eq.C-4), into our original equation C-1 without the integral term, we obtain:

\[
\frac{\varphi_{k}^{n+1} - \varphi_{k}^{n}}{2 \Delta t} = F + D \frac{\varphi_{k+1}^{n} - 2 \varphi_{k}^{n} + \varphi_{k-1}^{n}}{(\Delta x)^2}
\]  

which we can rearrange as:

\[
\varphi_{k}^{n+1} = \varphi_{k}^{n} + 2 \Delta t \left[ F + D \frac{\varphi_{k+1}^{n} - 2 \varphi_{k}^{n} + \varphi_{k-1}^{n}}{(\Delta x)^2} \right]
\]
This equation defines an *explicit scheme* for solving the 1D like-diffusion problem. We can use this scheme to explicitly compute all $\varphi_{n+1}^k$ given values from the previous time step ($\varphi_n^k$). Finally, we also need to discretize the initial and boundary conditions of Eq.(C-1). In this case, the conditions are written as:

\[
\begin{align*}
\varphi_0^k &= f(k\Delta x), \quad k = 0, \ldots, M. \\
\varphi_0^{n+1} &= 0, \quad n = 0, \ldots, N. \\
\varphi_M^{n+1} &= 0, \quad n = 0, \ldots, N.
\end{align*}
\]

Notice that for the boundary conditions, we write the expressions for $\varphi_k^{n+1}$ not $\varphi_n^n$. The basic structure of the solution method for Eq.(C-1) is schematized in Fig.(1).

It can be demonstrated that in order for the solution of Eq.(C-6) to be stable, the condition $\frac{D\Delta t}{(\Delta x)^2} < \frac{1}{2}$ must be fulfilled [117,118].

In the Initialize() subroutine, we set the values of parameters (e.g., the diffusion coefficient $D$, the driving force $F$, the grid-spacing $\Delta x$, $\Delta t$, etc.), construct an array or matrix to store the values $\varphi_k^n$, and apply the initial condition $f(k\Delta x) = 0$ for each $k$. At this point it is important to set the total current (defined in $F$) only between the current contacts and
the correct direction of the pinning field $E_p$, defined also in $F$. Beyond the current contacts, $j_{total} = 0$.

Once initialization is complete, we commence a for-loop to step through the $n = 0, ..., N$ time steps at which we seek to compute the solution. The Evolve_One_Time_step() subroutine then computes new values $\varphi_k^{n+1}$ for all $k = 0, ..., M$ grid points using the discretized Eq.(C-6) and the boundary conditions given by equations C-8 and C-9.

Notice that the appropriate choice of the $N$ determines the period of the driving force. Every time the solution is found for a time step, the phase-slip term must be added at each position along the length $L$.

Once the solution is found for the entire time interval (half period) $(N\Delta t)$, the current is reversed and the initial condition is modified to $f(kx\Delta) = \varphi_k^{N\Delta t}$ for all $k = 0, ..., M$ and the entire process is repeated until the phase becomes periodic in time for all spatial points within $0 < x < L$, this part is done by the Periodicity_Phase_Profiles() subroutine.

The Output_Results() subroutine took different forms. For example, we either wrote the current solutions $\varphi_k^{n+1}$ to a file for later analysis or plotted the solutions in a graphical window i.e. real-time visualization.

Once we computed the spatial profile for the phase, for a entire period, we proceeded to compute numerically the first Fourier component of the strain at different positions and for different values of current.

Finally, the program was implemented using Python that is a dynamic object-oriented programming language. It offers strong support for integration with other tools and comes with extensive standard mathematical libraries. Gnuplot and Pylab were the tools used to visualize huge amount of data generated on-the-fly. Numpy and Scipy are the two main libraries of algorithms and mathematical tools for the Python programming language. For a comprehensive review of the integrations of these tools with Python, see Ref [117]. Sigmaplot and Origin were used mainly to fit the data.
Bibliography


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