Dynamical Phase Transitions in Electronic Systems Induced by Optical or Voltage Pulses

Examples of a phenomenological theory.

The program:

1. Manipulating discommensurations - TaS2. Intrinsic inhomogeneities.
2. Patterns formation for pumped excitons: remind N. Kirova talk.
3. Historic excursion to the most (the only ?) clear (?) case of dynamical phase transition: CDW, effects of enforced inhomogeneities.
4. Stripes aggregation for pumped solitons:
   recall Poster I-2 stand or P. Karpov and SB, PRB-2016
Theories of temporal processes in out-of-equilibrium strongly correlated electronic systems:

1. *Ab initio* calculations or many-body approximations for microscopic models: highly challenging difficulties, great efforts, very useful results. Limitation to small # of particles even in 1D, problem of energy release.

2. Phenomenological approach for regimes governed by collective variables like order parameters for electrons and lattice deformations. It becomes indispensable for spacio-inhomogeneous regimes with patterns formation. It allows to approach coherent dynamics of macroscopic electronic order through a symmetry breaking transition, to recover dynamical symmetry breaking, stratification in domains, etc. It is always correct within its applicability, but it may not come rightly: the quasi-equilibrium regimes may be reached only after the most interesting events had happened.
I. Understanding the route to the hidden phase in TaS2
1T-TaS2 – microscopic foundations (partly our view, disputable).

**Background:** narrow-gap ($E_g = \Delta_e + \Delta_h \approx 0.8eV$) insulator formed from parent metal (with 1e per Ta site) by a high-T (>500K) CDW.

Incomplete nesting leaves each 13-th electron ungaped which in a typical CDWs would give rise to a pocket of carriers.

Here, each excess carrier is self-trapped by inwards displacements of the surrounding atomic hexagon (forming the “David star” unit) which gives rise to the intragap local level accommodating this electron.

These charged **heavy polarons** inevitably arrange into the **Wigner crystal – WC**. which is always a hexagonal super-lattice – here, by Nature chance, upon the underlying also hexagonal lattice.

This ideal locked form is the commensurate C phase.
Exciting the self-trapped electron from the intragap level deprives the deformations from reasons of existence, the David star levels out in favor of a void in the WC while the electron has been sent to a higher delocalized band.

Adding an electron to the UHB may lead to a stable bipolaron, but the repulsion energy cost most probably will not allow for its stability. Mitosis into two polarons will proceed thus creating an interstitial in the WC – both voids and interstitials have been seen by STM.
Phase separation: voids are expelled in-between dense clusters yielding the near-commensurate NC phase.

\[ \frac{d\mu}{dn} < 0 \]

If not expelled, then the WC melting gives rise to the IC phase seen at higher T.

\[ \frac{d\mu}{dn} > 0 \]

Again! that depends on the curvature sign of the free energy \( d^2F/dn^2 \)

Such a self-tuned Wigner-Mott state stays always, even under doping, in half-filled Mott insulator regime: number of sites is regulated to adjust to the number of electrons. (common notion in CDWs where #periods=2#electrons).

There cannot be such a thing here as the dopped MI; this is a WC with (expelled) defects.
Astonishing success while no inputs from electronic bands, correlations and Mott state, Ta-S ions interactions, etc. A triumph of phenomenology but at a forbidden price of high (up to 60) harmonics per each CDW. The reason and the key to the upper theory: narrow domain walls.
Networks of walls appear locally after the strong pulse from the STM tip and measured then by the same STM. After H.W. Yeom group (left) and D. Mihailovic group (right). Most of walls are lines of missed David stars, hence insulating. Their number determines the concentration of defects – aggregated voids – working as dopants. Their concentration yields the electron-hole imbalance.
Phenomenology starts as a guess for the free energy as a function of defects concentration $F_d(n_d)$.

That could be any double-well curve for the energy to give rise to a $1^{\text{st}}$ order C-IC transition – the experimental fact.

We narrow the choice applying the qualitative theory for incommensurable superlattices by Bak and Villain where the $1^{\text{st}}$ order is explained as effect of crossings of domain walls.

$F_d$ and the chemical potential $\mu_d = \frac{dF_d}{dn_d}$ as functions of defects concentration. Notice the cusp – not the generic smooth minimum at $n_d \to 0$ – initial doping of C phase.
$F_d (n_d)$ is the basic energy of the NC state with respect to the C one.

$C_0 < 1$ drives the NC instability at $C_0 < 0$  

$C_1$ -- stabilizing DWs repulsion

$F_d(n_d) = E_{DW}(C_0 |n_d| + C_1 |n_d|e^{-1/(\xi |n_d|)} - C_2 \xi n_d^2 + C_4 \xi^3 n_d^4)$

Energy $< 0$ of DW crossings  
Repulsion of crossings

Here $n_d$ is the concentration of voids aggregated into walls. Otherwise, in the IC phase, $n_d = n(\text{voids}) - n(\text{interstitials})$.

In any case, the conservation law of electrons:

$n_e - n_h = n_v - n_i = n_d$
Chemical potential surfaces: $-\mu_e(n_e)$, $\mu_h(n_h)$, $\mu_d(n_e-n_h)$ and lines of their intersections – pairwise partial equilibria. C,U,H are triple intersections where $-\mu_e(n_e)=\mu_h(n_h)=\mu_d(n_e-n_h)$. C ($n_e=n_h$, $n_d=0$) and H are local equilibria. Point U of the energy maximum is repulsive.

Variations of parameters and temperature can change plot's topology.
Rates eqs. for concentrations are designed minimalistically - just to satisfy the requirement that binary rates pass through zero when chemical potentials become equal.

\[
\frac{dn_{\text{h}}}{dt} = -k_{\text{eh}}n_{\text{e}}n_{\text{h}}(\mu_{\text{e}} + \mu_{\text{h}}) - k_{\text{hd}}n_{\text{h}}(\mu_{\text{h}} - \mu_{\text{d}}) + P(t)
\]

\[
\frac{dn_{\text{e}}}{dt} = -k_{\text{eh}}n_{\text{e}}n_{\text{h}}(\mu_{\text{e}} + \mu_{\text{h}}) - k_{\text{ed}}n_{\text{e}}(\mu_{\text{e}} + \mu_{\text{d}}) + P(t)
\]

Here \( k_{ij} \) are just constants but they may be \( T \)-dependent. \( \mu_i = \mu_i(n_i, T) \) are \( T \)-dependent for sure, so a need to add an eq. for the evolution of \( T \rightarrow T_{\text{e}}(t) \) – the electronic temperature. \( T \) branches to the electronic \( T_{\text{e}} \) for \( \mu_{\text{e}}, \mu_{\text{h}} \) and the lattice one for \( \mu_{\text{d}} \)
Trajectories - parametric plots of $n_e(t)$ and $n_h(t)$ superimposed on lines of partial equilibriums given by intersections $\mu_e = -\mu_d$, $\mu_h = \mu_d$, $\mu_e = -\mu_h$ - drawn for the final temperature after the system has stabilized.

A: Above the switching threshold $U > U_T$ - reaching the H-state

B: Below threshold $U < U_T$. The system returns to the C state.

C: Erasure by heating in the H-state. Trajectory first leaves the H-point, then joins the commensurate line. After reaching a maximum $C'$, on cooling the system returns to point C.
The moment of truth: tr-ARPES of the H phase, after Patrick S Kirchmann (Stanford, unpublished)

“trARPES suggest that e-h imbalance drives switching”

- e-h imbalance near threshold drives switching
- agrees qualitatively with phenomenological model by Serguei Brazovskii
Instability towards stripe formation in 1T-TaS2 after charge injection.

Following the previous talk and the publication

A generic bistable system in-between two contacts. Commonly, a potential applied to a sample is expected to concentrate the local charge density near the contacts so that charge is screened. In our special situation the charge penetrates into the bulk of a bistable medium in which the competition of phases is controlled by the particle density $n$, here it is $n_d$. 
Thermodynamic quantities as functions of $n$ for bi-stable systems near the 1st order phase transition: free energy $E$ (brown), chemical potential $\mu$ (red), its derivative $k$ (blue-dashed).

b: $E(n)$ at small $n$ has a cusp, it starts as $E \propto n$ and then slows down. $E(n)$ is concave around the low $n$ C phase: the compressibility is negative $k = d\mu/dn < 0$ for all $n$ up to the inflection point of $E(n)$ which lies between the barrier and the high $n$ minimum.
For a charged system, this violation of the stability criterion means that the screening length square becomes negative

\[ \left( \frac{1}{l_{\text{scr}}} \right)^2 = 4\pi e^2 \left( \frac{dn}{d\mu} \right) < 0 \]

Then \( l_{\text{scr}} \) becomes imaginary. That leads to oscillations instead of the conventional exponential decay with distance, resulting in phase separation and stripes formation.

For our nonlinear system, this feature is hidden in eqs. for the density \( n(x) \) and the electric potential \( \Phi(x) \) which we solve numerically

\[ \mu_{\text{tot}}(x) = \mu(n(x)) + e\Phi(x), \quad \varepsilon_0 \Phi'' = -4\pi en_3 \]

\[ j(x) = -\sigma(n(x)) \partial_x \mu_{\text{tot}}(x) = j = \text{const} \]
Undulations between “hole-doped” and “electron-doped” domains, $n > 0$ and $n < 0$.

With increasing $j$, patterns evolve from a nearly sinusoidal shape to sharp domains whose number decreases progressively, until the last strong one remains near the contact at $x=1$ ($x=0$ is the middle of the sample) while the bulk is converted to a highly conducting state with smooth and weak undulations.

At low $j$, the period does not vary much with $j$ and stays close to the intrinsic value $\sim 2\pi l_{scr}$. 

$x=0$, sample’s middle $\quad x=1$, sample’s edge
Summary for part I.

TaS2 as a self-tuned, phase-separated, always filled, Mott state of a Wigner crystal of polarons, swallowing excited holes as vacancies, then expelling them out to form the net of domain walls.

Mutual transformations among the three reservoirs: electrons, holes, defects are dictated by imbalances of partial chemical potentials. The e-h compensated just pumped C state evolves into the noncompensated (self-doped) H state.

Walls crossings are responsible for the free energy form yielding the $1^{st}$ order phase transition and the screening instability: undulating penetration of the electric field into the bulk under the applied current.

Incompleteness of the presented phenomenological approach: It is over-coarse-grained, averaged over the network of domain walls. Need to descend to the single-wall, single-node level. Descriptions of optically- and current-induced routs to the hidden phase are not well connected yet.
III. Intrinsic inhomogeneities: stratification, phase separation, domains

Pumping to excitons, implying charge-transfer systems, inspired by neutral-ionic transition. (N. Kirova talk)

\[ \frac{dV}{dq} = \frac{d^2W}{dq^2} < 0 \]

The free energy \( W(q) \) starts linearly \( W \propto q \) and continues with the negative curvature - expecting the barrier ahead on the way to another (meta)stable state. This basic notion was sufficient to obtain the stratification and local amplification leading to subcritical PIPT.

Space-time modeling: self-focusing, nucleation and divergence of domains, their reflection and merging
The minimal model for the CTE interacting with the symmetry breaking order. The energy $W(q,h)$:

$$W = E_{ex} q + \frac{a}{2} q^2 + \frac{b}{3} q^3 + \frac{c}{2} \left( \frac{q}{q_c} - 1 \right) h^2 + \frac{f}{4} h^4$$

$q$ – charge transfer

$= \text{excitons’ density}$

$h$ – lattice deformation

$q_c$ – critical value of $q$ to initiate $h$

Energy $W(q,h) \rightarrow W^*(q)$ and the potential $V(q,h) \rightarrow V^*(q)$ after minimization over $h$. $V=dW/dq$

4 intervals of $q$: repulsion, attraction, creation, repulsion of excitons
**Supercritical pumping:** $q$ rises above the initial pumping level by generation of excitons from the vacuum.

**$S=0$:** $q$ and $h$ reach smoothly the equilibrium values of the EI state. $\phi$ also saturates ($E_{ex} \to 0$!) at an arbitrary value.

**$S \neq 0$:** stronger and unharmonic oscillations at intermediate times. Sharp lock-in transition of phase spikes new set of strong oscillations.

\[
\Delta W = \frac{1}{2} (S^{*} \Psi^{2} + S \Psi^{*2}) = |S| q \cos 2(\phi - \alpha)
\]
IV. To justify an efficiency of a phenomenology, make a history excursion. A rare case where both the phenomenology is applicable and the underlying microscopics is controlled:

NON EQUILIBRIUM COHERENT DYNAMICS IN CHARGE DENSITY WAVES FROM FEMTO-SECOND OPTICAL EXPERIMENTS AND THEIR MODELING.

Theory versus Experiment

Spectral density of the CDW amplitude mode after the distracting pulse. 
Red arrows – dynamical phase transition restoring a symmetry breaking. 
WHITE ARROWS – 
Annihilations of domains alternating in depth of the sample.

Numerical modeling

Experimental spectrum
Time evolution of the ground state energy profile as function of the order parameter. Red dot - the system state.

1. Starting state at t<0: symmetry broken, at one of allowed minima.
2. After the distraction: no more nontrivial energy minimum, the high energy with respect to the new profile initiates pendulum oscillations.
3. Friction reduces the energy of oscillations. The relaxation of non-equilibrium fermions allows to work out nontrivial minima – still too shallow with respect to oscillations energy.
4. Approaching the dynamical phase transition. The decreasing energy and the growing barrier meet each other.
5. Trapping to one of possible the symmetry broken states. Gradually vanishing oscillations near the new state.
Decreasing intensity of the destruction pulse in the sample depth → trapping to different equivalent states → domain structure.

Spacio-temporal modeling with experimental parameters:

Collapse of domains by annihilation of domain walls.

Ripples in the space-time texture are due to annihilation events.
V. The solitons start coming to our eyes like pokemons: hunt them

SRM: Dimerized Peierls state of Indium chains on Si, T.H. Kim and H.W. Yeom

CDW in NbSe₃, Defected chain STM vs theory Brun, Wang, Monceau & SB

P. Karpov & SB
Poster I-2
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Phase diagram of 3D system in temperature-concentration coordinates. The region under the red curve is the phase of confined bisolitons (the long-range ordered phase). The trajectory of cooling and relaxation (brown) after the optical pump (green) crosses two transition lines.

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A few inequalities which frame our school

\# of IMPACT meetings > 1

\# of IMPACT participants > 100

\[ \frac{dn}{d\mu} < 0 \]