Incorporating Decoherence in the Dynamic Disorder Model of Crystalline Organic Semiconductors

Wei Si*, Yao Yao and Chang-Qin Wu

State Key Laboratory of Surface Physics and Department of Physics, Fudan University

I. Introduction

- Organic field effect transistors (OFET) based on organic semiconductors (OSC)
  - ✓ Promising candidates for future printing electronics.
  - ✓ Improving quality of OSC -> Intrinsic transport regime
- Feature of charge transport in crystalline OSC
  - ✓ Tunable temperature dependence of mobility [1]
  - ✓ Electronic states taking part in the transport localized to ~10 molecules [2]

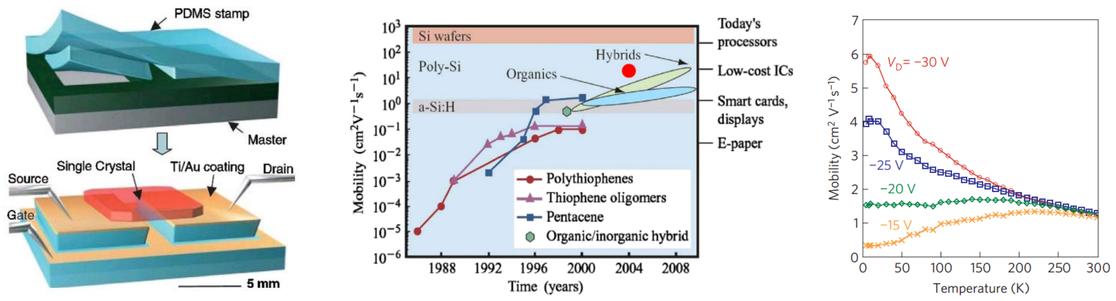


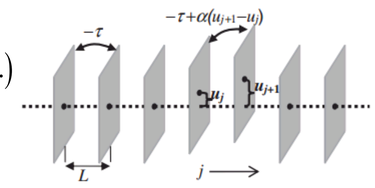
Figure. Left: structure of OFET; Middle: Improving mobility of OSC;
Right: typical temperature dependence of mobility in crystalline OSC [1]

II. Dynamic Disorder Model

- The strong electron-phonon coupling plays a central role.
  - ✓ Holstein type: coupling through tuning the on-site energy
  - ✓ SSH type: coupling through tuning the transfer integral between sites
  - ✓ In OSC, the SSH type is thought to be important and is studied below
- One promising model is the dynamic disorder model proposed by Troisi *etc.* [2]
  - ✓ Quantum electrons + classical lattice vibrations -> Coupled non-adiabatic dynamics
  - ✓ Random displacements from temperature effects -> localization of electronic states
  - ✓ Dynamic disorder -> Break the localization -> Transport

$$\hat{H}_{\mathrm{el}} = \sum_j \left[-\tau + \alpha\left(u_{j+1} - u_j\right)\right]\left(\hat{c}_{j+1}^{\dagger} c_j + \mathrm{h.c.}\right)$$

$$H_{\mathrm{la}} = \sum_j \left(\frac{1}{2} m\dot{u}_j^2 + \frac{1}{2} K u_j^2\right)$$



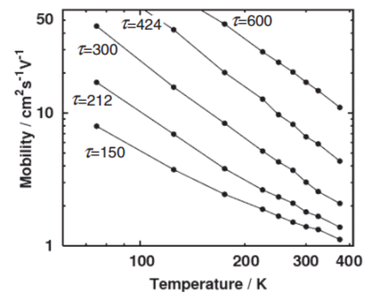


Figure. Left: illustration of the dynamic disorder model;
Right: temperature dependence of mobility from the model

III. A consistent physical picture

- Problem 1: the diffusion constant grows in the long time regime [3]
  - ✓ Could be overcome by introducing relaxation time to the velocity correlation function
- Problem 2: coherent evolution leads to de-localization
- Desirable physical picture: two-fold role of phonons
  - ✓ Coupling with low-frequency ones: help break the localization
  - ✓ Coupling with high-frequency ones: decoherence of the electronic state

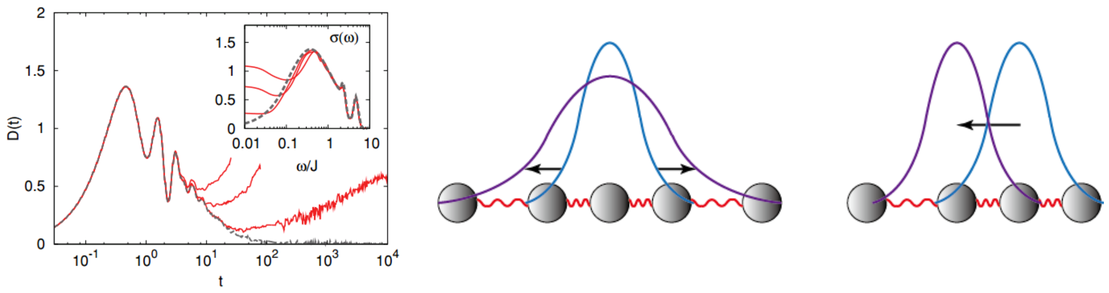
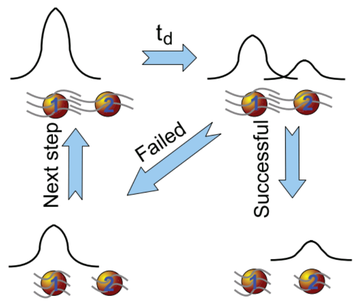
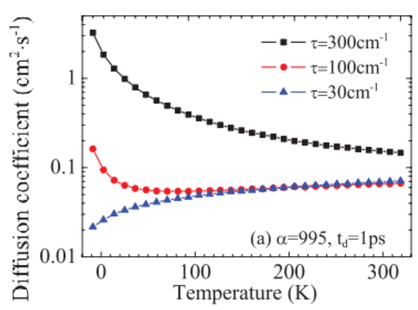


Figure. Left: growing diffusion constant with time;
Middle and right: two-fold role of phonons in the desirable physical picture

IV. Decoherence in the Site Basis

- Collapsing the state to a certain site after each decoherence time t_d
  - ✓ The probability to hop to a certain site decided by the population of electronic state
  - ✓ Band-like to hopping-like behavior of mobility with decreasing transfer integral
  - ✓ Could overcome the problem of growing diffusion constant
- Problem: not feasible to define a localization length of the electronic state





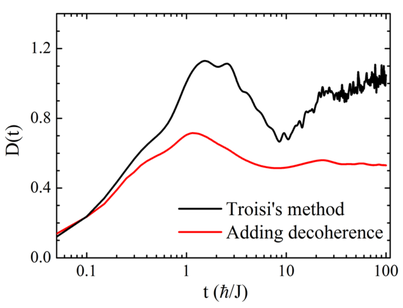


Figure. Left: illustration of decoherence in the site basis; Middle: resulting behavior of mobility; Right: the growing trend of the diffusion constant is overcome

V. Energy-based Decoherence Correction (EDC)

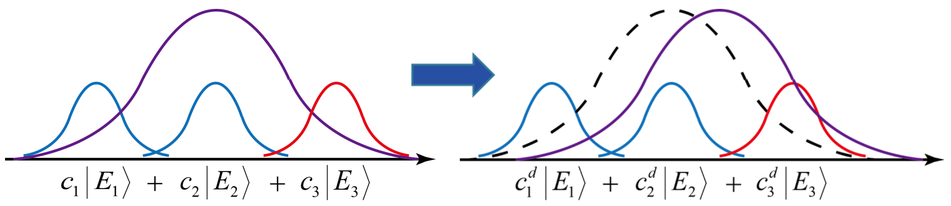
- In retrospect of the above issues, we further choose the EDC method [5]
  - ✓ Evolve the system by a time step Δt;
  - ✓ Expand the state by instantaneous eigenstates $|\psi(t)\rangle = \sum_j c_j |E_j(t)\rangle$;
  - ✓ Pick the current state $|E_i(t)\rangle$ with $\sum_{j=1}^{i-1} |c_j|^2 < \xi \leq \sum_{j=1}^{i} |c_j|^2$, where ξ is a random number;
  - ✓ Rescale the expansion coefficients according to the decoherence time τ_{ij} by

$$c_j^d = c_j \exp(-\Delta t/\tau_{ij}) \text{ for } j \neq i \text{ and } c_i^d = c_i \left(\frac{1-\sum_{j\neq i}|c_j'|^2}{|c_i|^2}\right)^{1/2}.$$

- The decoherence time τ_{ij} takes the common form used in surface hopping studies

$$\tau_{ij} = \frac{\hbar}{|E_i(t) - E_j(t)|}\left(C + \frac{E_0}{E_{\mathrm{kin}}(t)}\right)$$

  - ✓ Parameter C is from coupling with high-frequency phonons and is material specific.



VI. Preliminary Results with the EDC

- EDC speeds up the diffusion process;
- Dynamic localization with tunable localization length

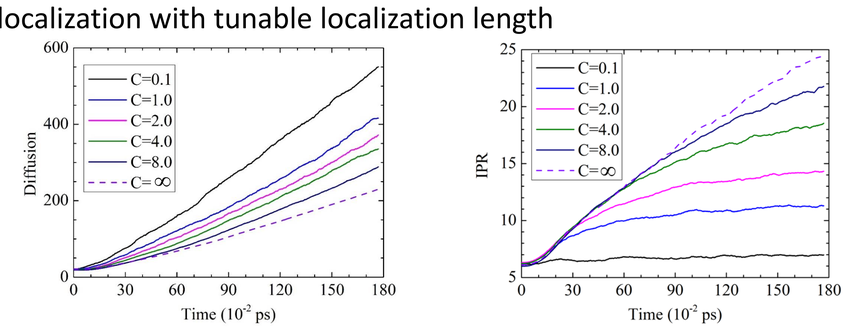


Figure. Diffusion and localization of the electronic state from the dynamic disorder model with EDC.

VI. Conclusion

We remark that the decoherence effects are essential for the self-consistency of the dynamic disorder model of crystalline organic semiconductors. They stem from the coupling of charge carriers with high-frequency phonons. By the method of decoherence in site basis, the mobility shows both the band-like and hopping-like behavior. We further introduce the energy-based decoherence correction into the model. The resulting dynamics shows a diffusion process of electronic states with finite localization length, which is the type of transport anticipated in such systems.

References

[1] T Sakanoue *et al.* Nature Mater. **9**, 736 (2010).
[2] K Marumoto *et al.* Phys. Rev. Lett. **97**, 256603 (2006).
[3] A Troisi *et al.* Phys. Rev. Lett. **96**, 086601 (2006).
[4] S Ciuchi *et. al.* Phys. Rev. B **83**, 081202(R) (2011).
[5] SC Cheng *et al.* J. Chem. Phys. **129**, 024112 (2008).
* 09110190003@fudan.edu.cn