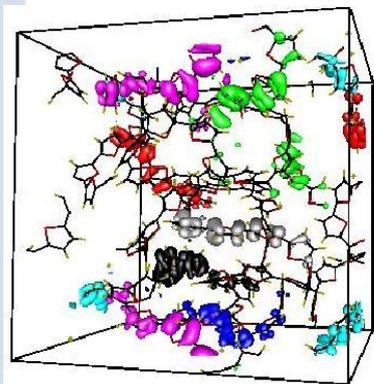
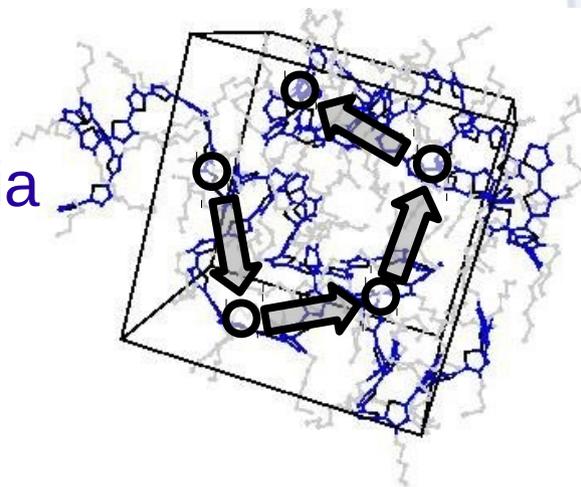


Multiscale Simulations of Charge Carrier THz Mobility in Conjugated Polymers



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Minisymposium on Time-Resolved THz and Microwave Spectroscopy,
19 September 2012, Lund, Sweden

Institute of Physics Belgrade

- **Founded in 1961.**
- **~100 PhDs.**
- **~100 PhD students.**



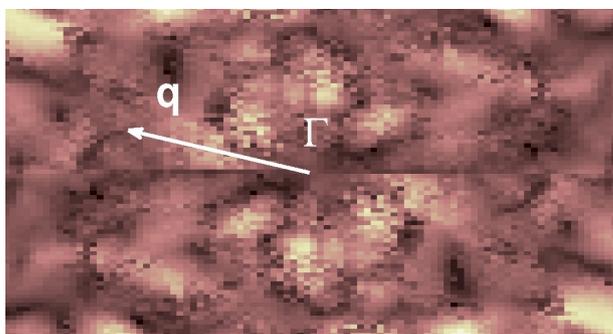
Scientific Computing Laboratory

- **Founded in 2005.**
- **Personnel**
 - **11 PhDs.**
 - **9 PhD students.**
- **Infrastructure**
 - **~1000 CPU cores, ~6 TFlops**
- **Simulations of complex systems:**
 - **Strongly-correlated systems**
 - **Bose-Einstein condensates**
 - **Granular materials**
 - **Organic materials**

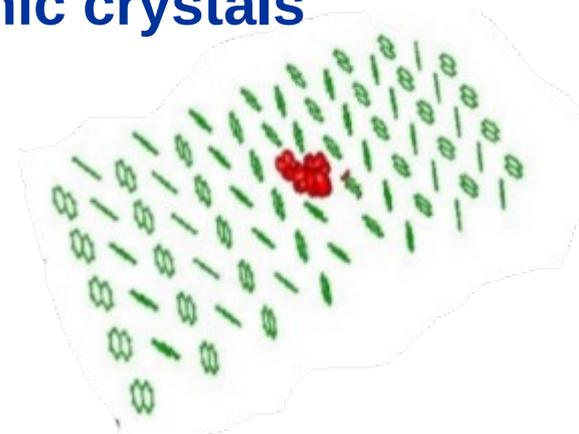


Simulations of electronic properties of organic materials

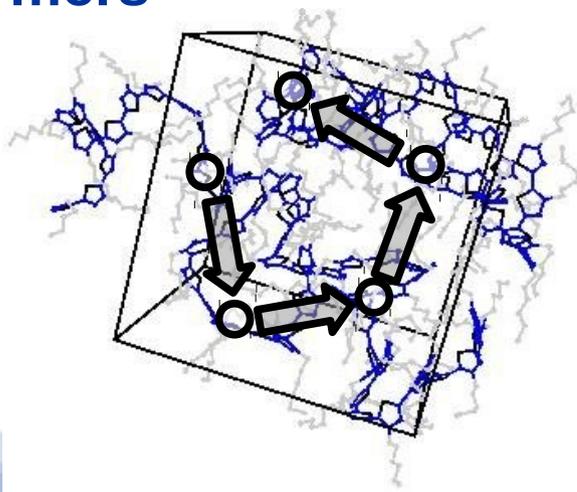
- E-ph coupling in organic crystals



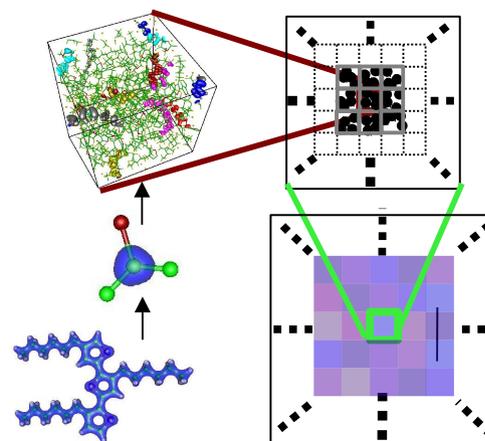
- Grain boundaries in organic crystals



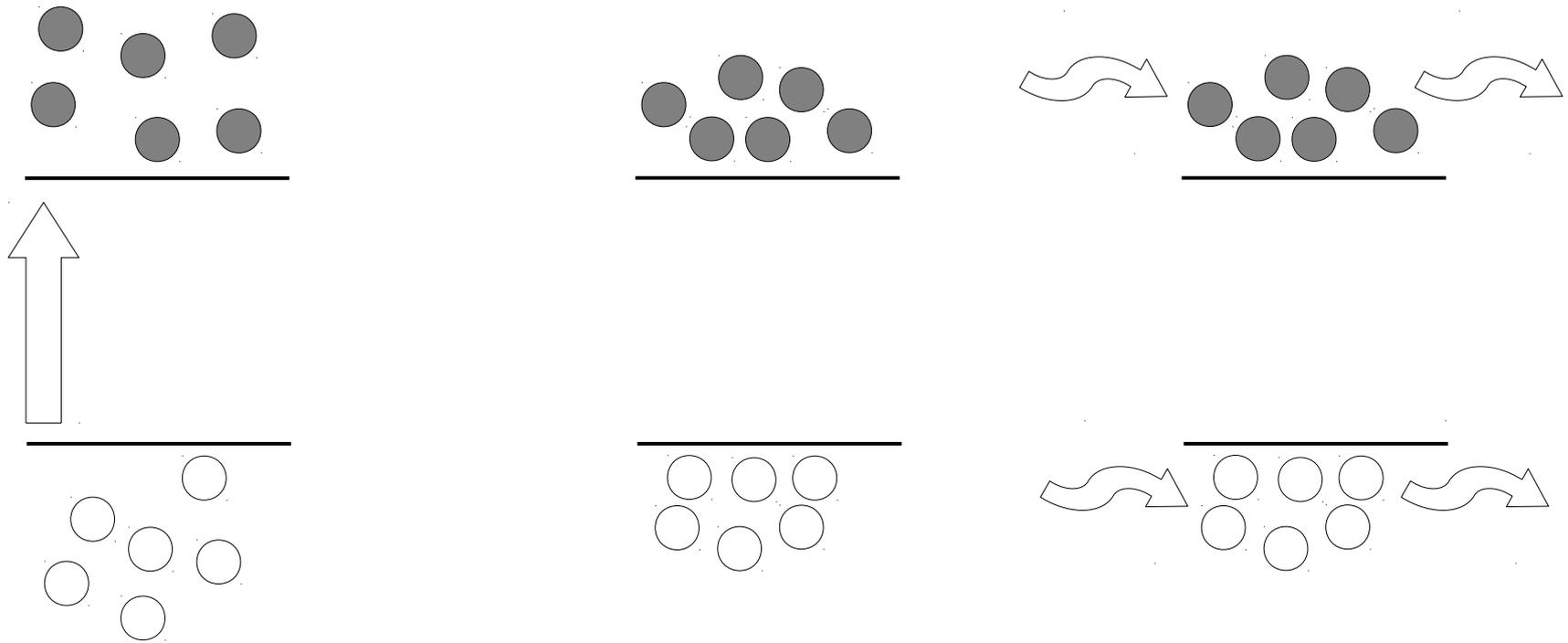
- Electronic structure and transport in disordered polymers



- Development of methods



Time-resolved THz spectroscopy



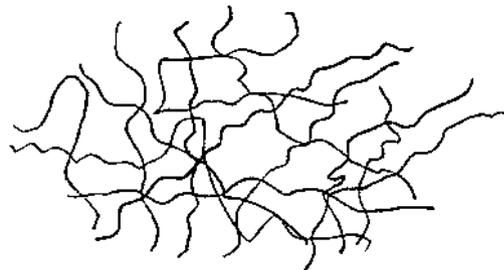
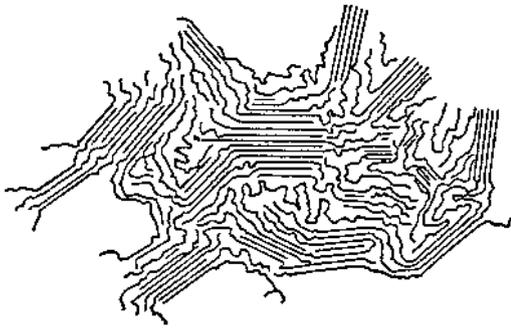
- Interaction with EM radiation (above-gap excitation)

- Charge carrier relaxation (including separation in BHJ)

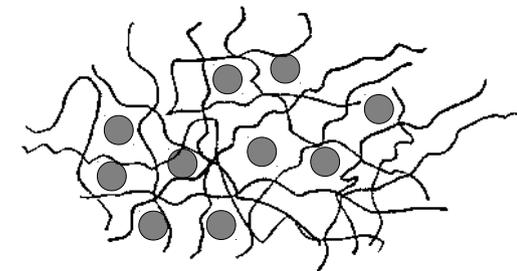
- Interaction with THz probe

Challenges in modelling/simulation of TR THz spectroscopy in organic materials

- Morphology of the material?



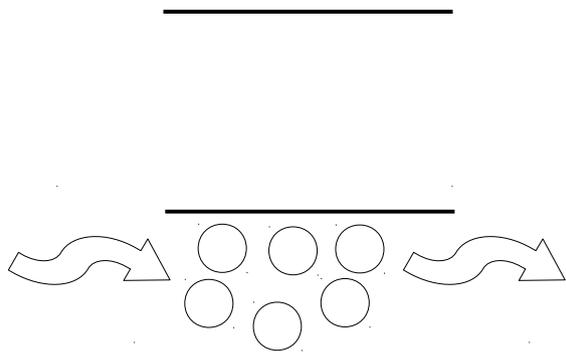
- Morphology of the donor-acceptor system?



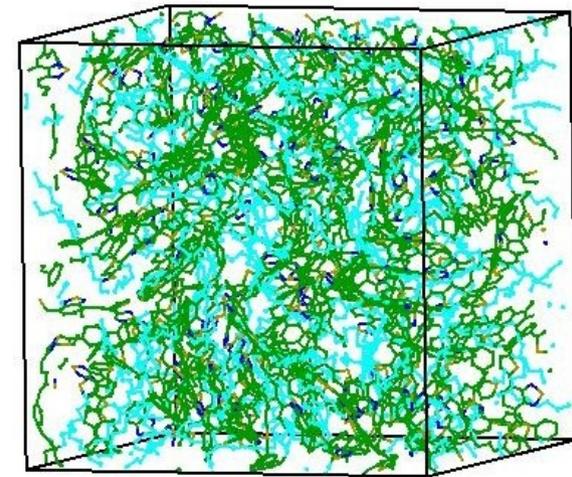
- Complex structure of the system
 - many theoretical approaches become impractical

THz mobility of holes in the polymer - assumptions

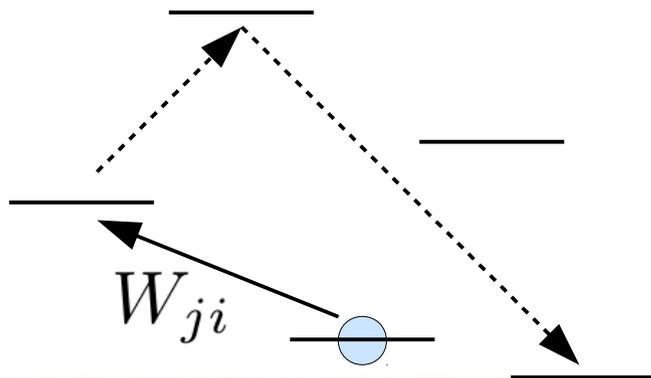
- Holes in polymer have reached thermal equilibrium.
- Low carrier density.



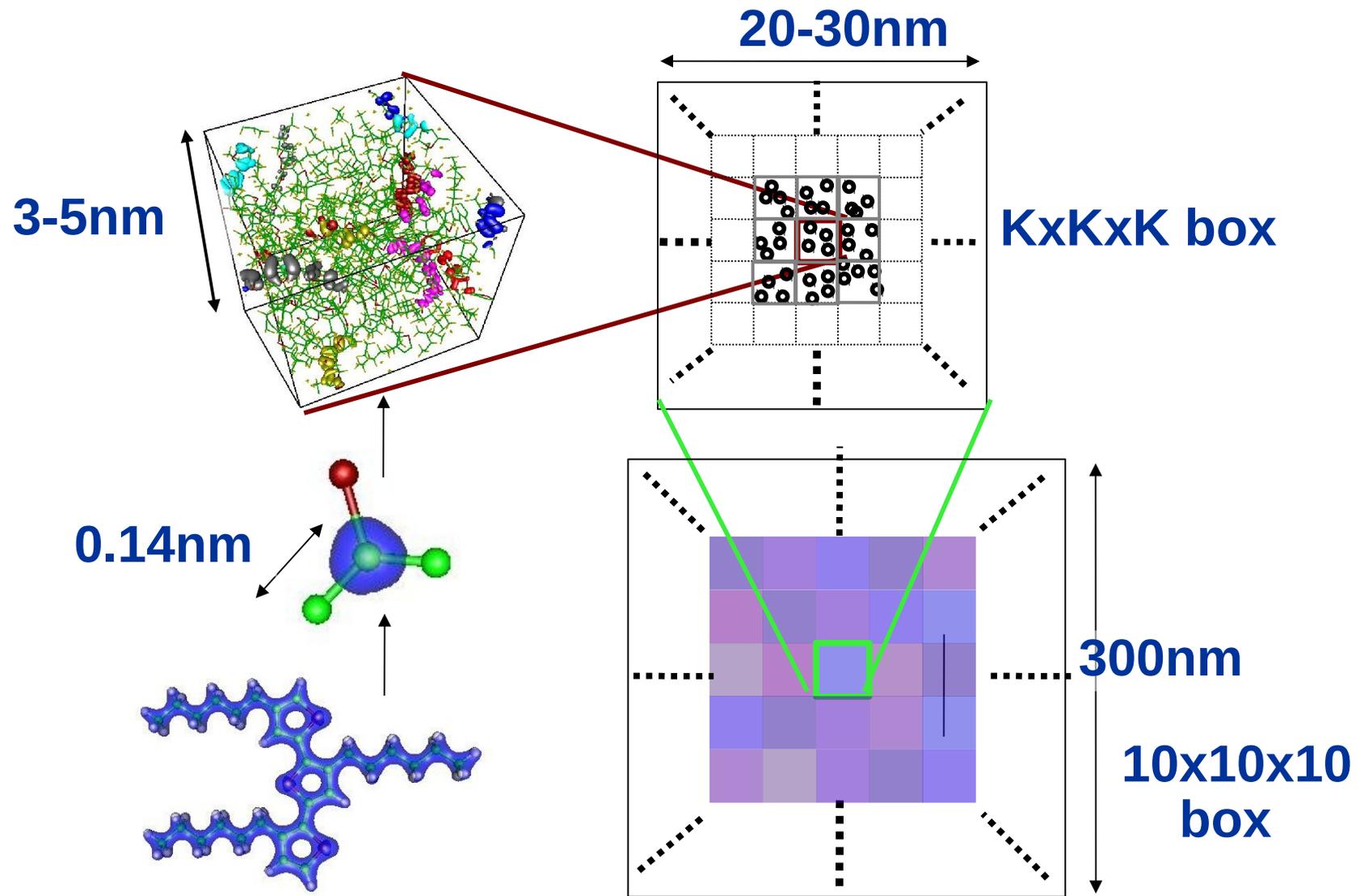
- Disordered morphology
 - Obtained from classical MD using simulated annealing



- Semiclassical charge transport.

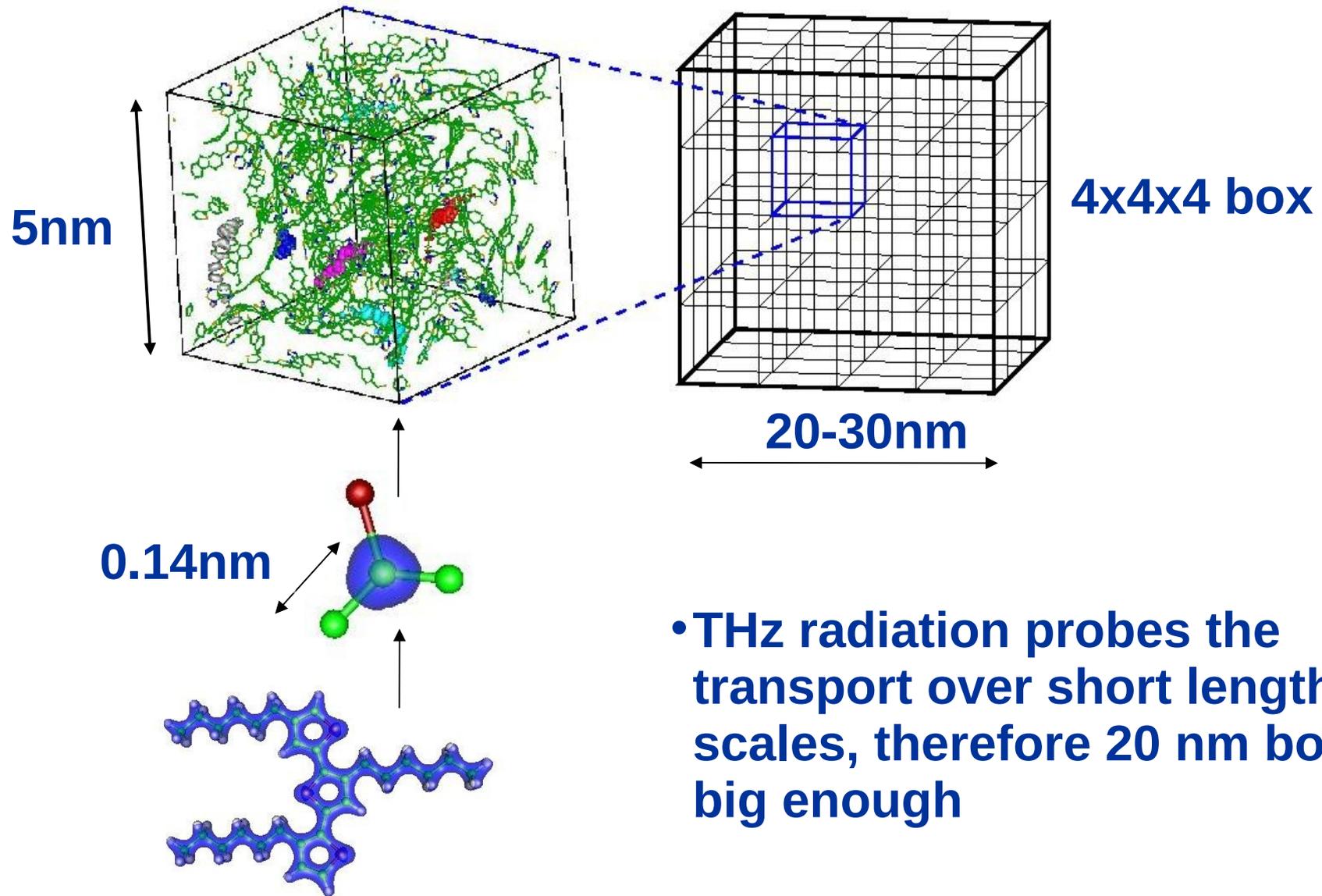


Multiscale method for DC carrier transport



N. Vukmirović and L.-W. Wang, Nano Lett. 9, 3996 (2009)

Multiscale method for THz carrier transport



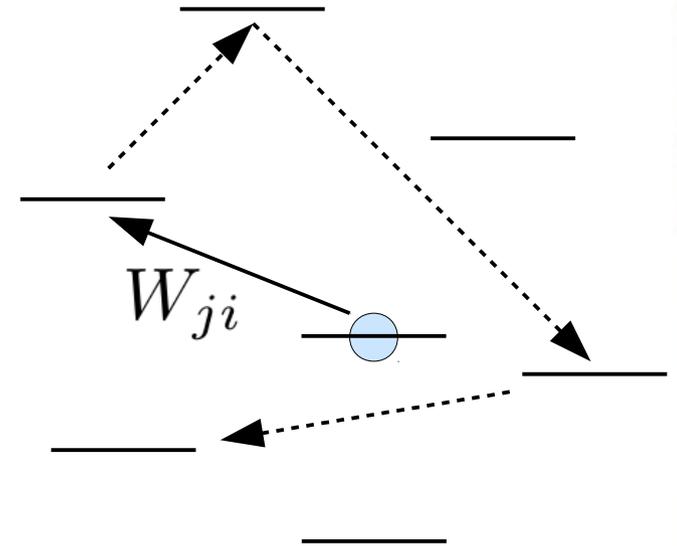
- THz radiation probes the transport over short length scales, therefore 20 nm box is big enough

Calculation of terahertz mobility

- Rate equations for populations of electronic states

$$\frac{dn_i}{dt} = \sum_j A_{ij} n_j$$

$$A_{ij} = W_{ji} - \delta_{ij} \sum_k W_{ik}$$



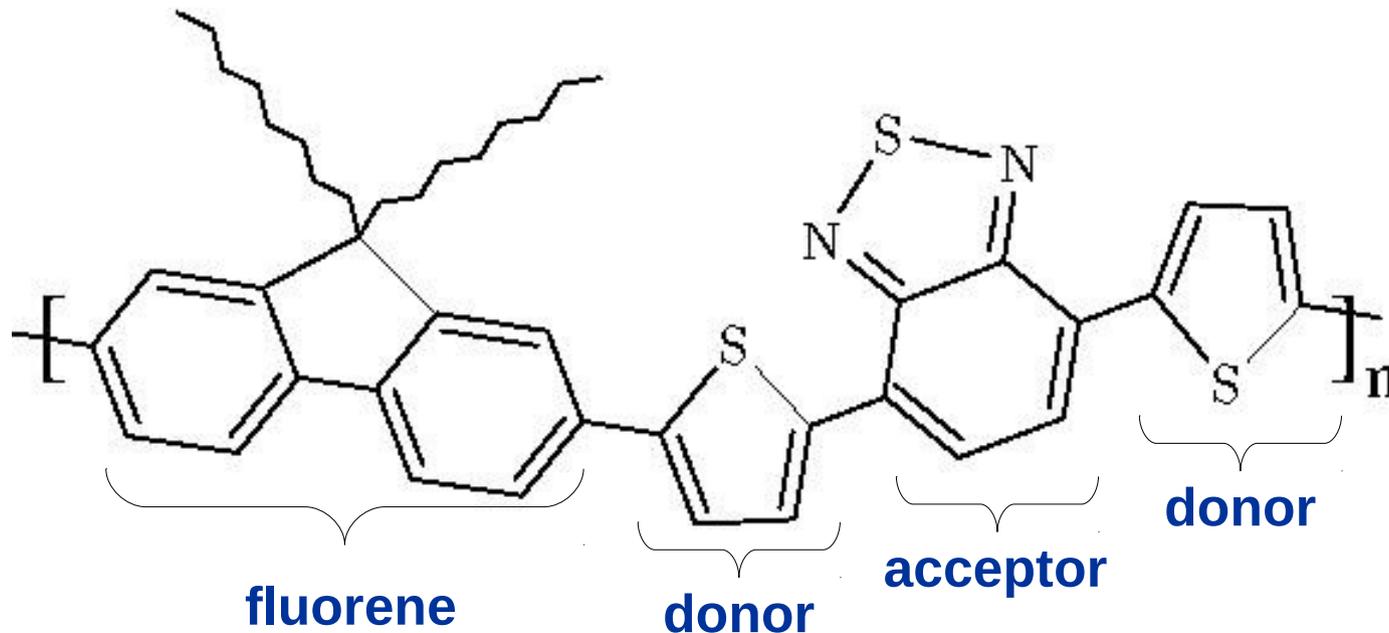
- Kubo's linear response formula

$$\mu(\omega) = -\frac{e\omega^2}{2k_B T} \int_0^\infty dt e^{i\omega t} \langle \Delta^2(t) \rangle$$

$$\mu(\omega) = -\frac{e\omega^2}{2k_B T} \sum_{i,a} w_a (\mathbf{R}_i - \mathbf{R}_a)^2 \left[(i\omega - [A])^{-1} \right]_{ia}$$

Polymer materials in this study

- Alternating polyfluorene (APFO-3)



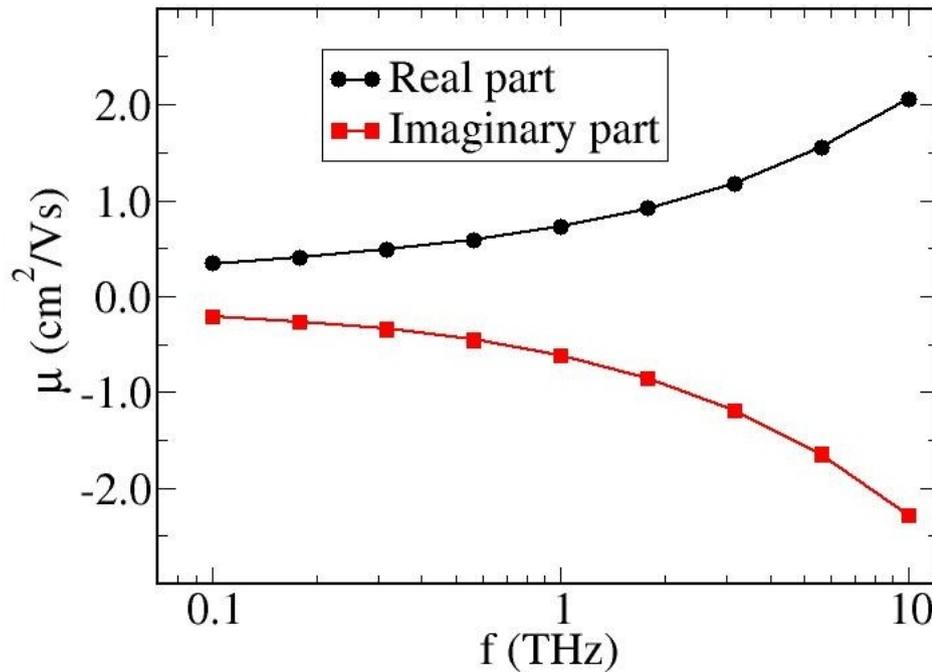
- Material in polymer and monomer form with and without alkyl side chains.
- Stiff – interring torsion barriers of 250 and 120 meV (vs. 80meV for P3HT).

Insights

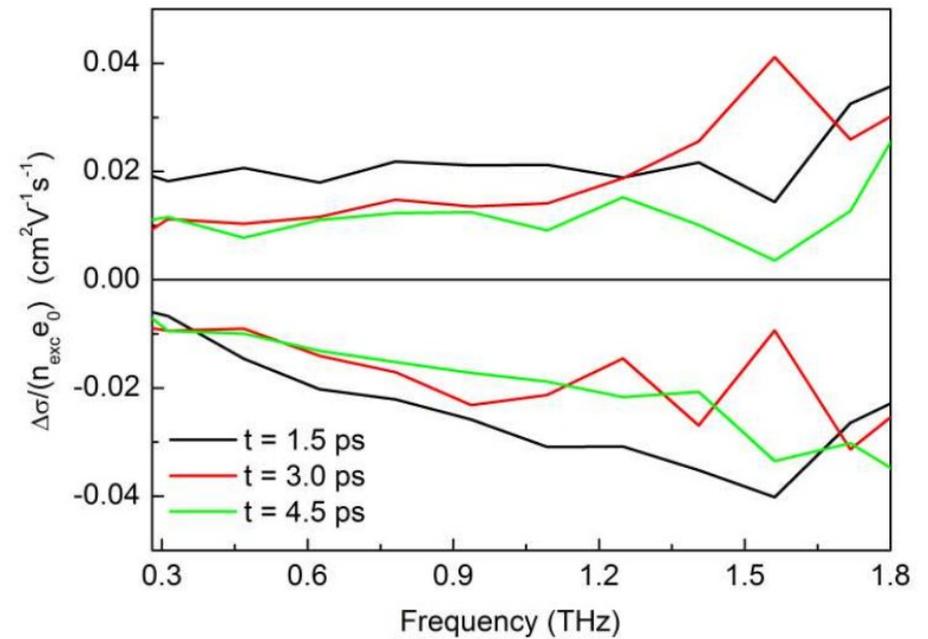
- **Identification of the origin of THz mobility**
 - **How far are carriers probed by THz radiation travelling?**
 - **What are they hopping times?**
- **Identification of parameters that affect the THz mobility**
 - **Energetic disorder**
 - **Temperature**
 - **Presence/absence of side chains**
- **Comparison with TR THz spectroscopy.**

Frequency dependence of mobility at 300K

- Hole mobility in APFO-3



simulation

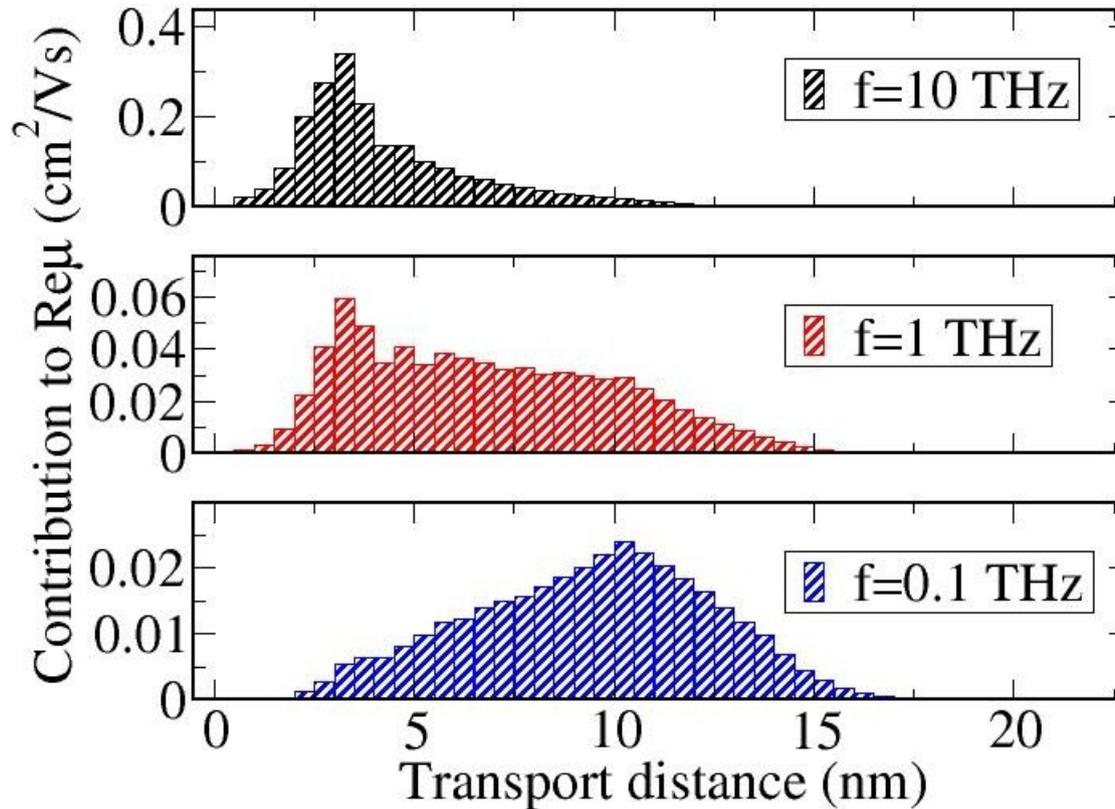


experiment

- The shape of the spectrum suggests that above THz hopping rates are present in the system.

What does THz radiation actually probe?

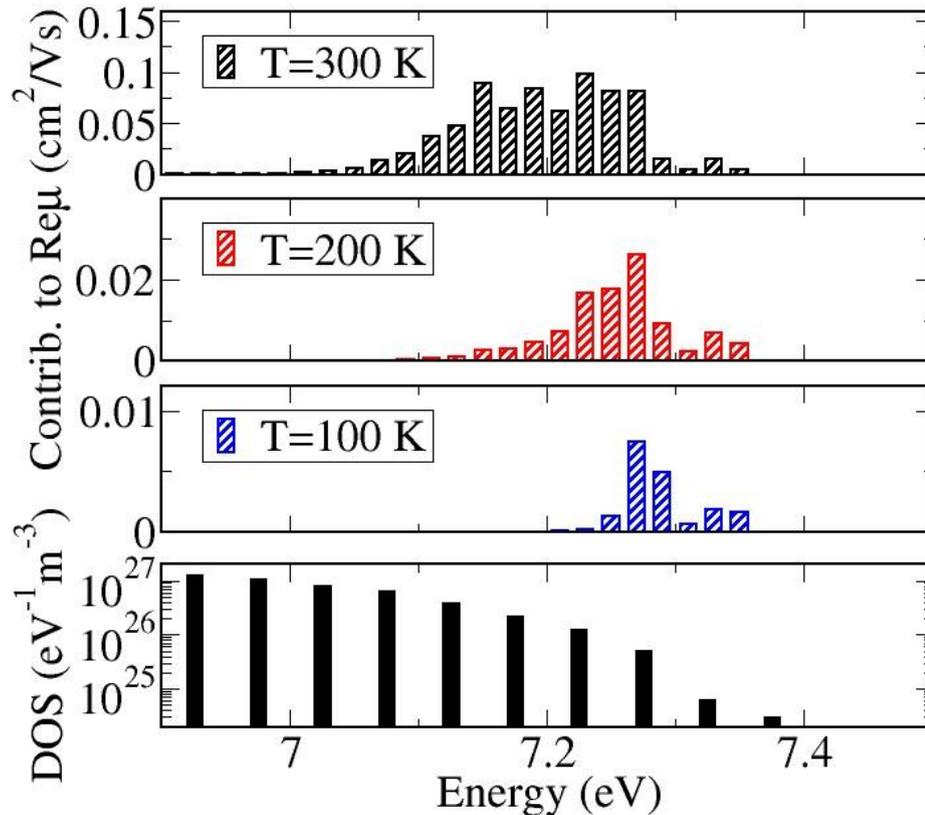
- Distance-resolved mobility:



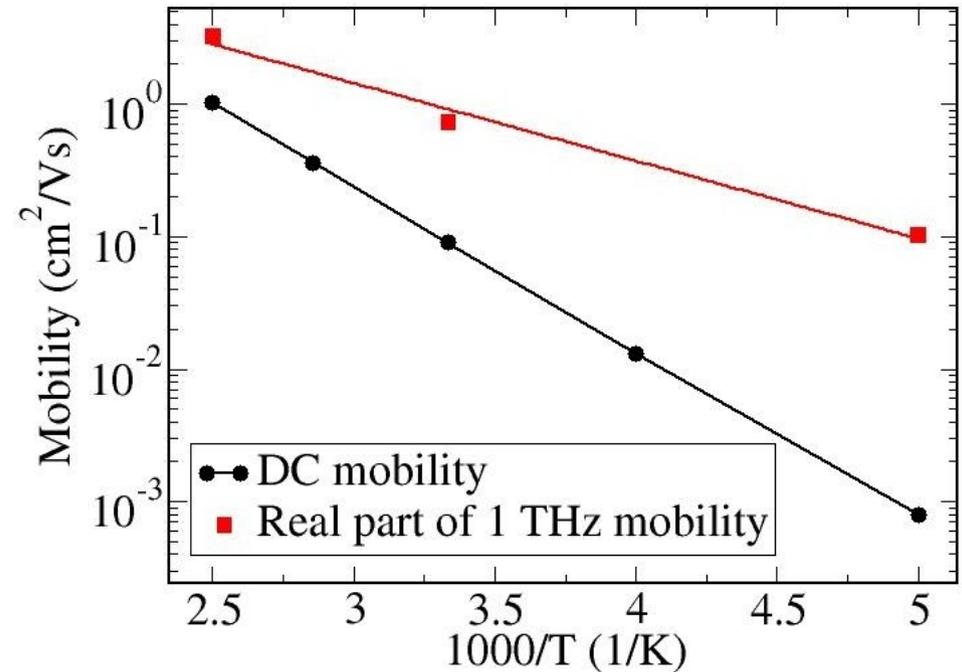
- High frequency (10 THz) – one or two hops are actually probed.
- Low frequency (0.1 THz) – transport over ~10nm is probed.

Temperature dependence of THz mobility

- Energy-resolved mobility

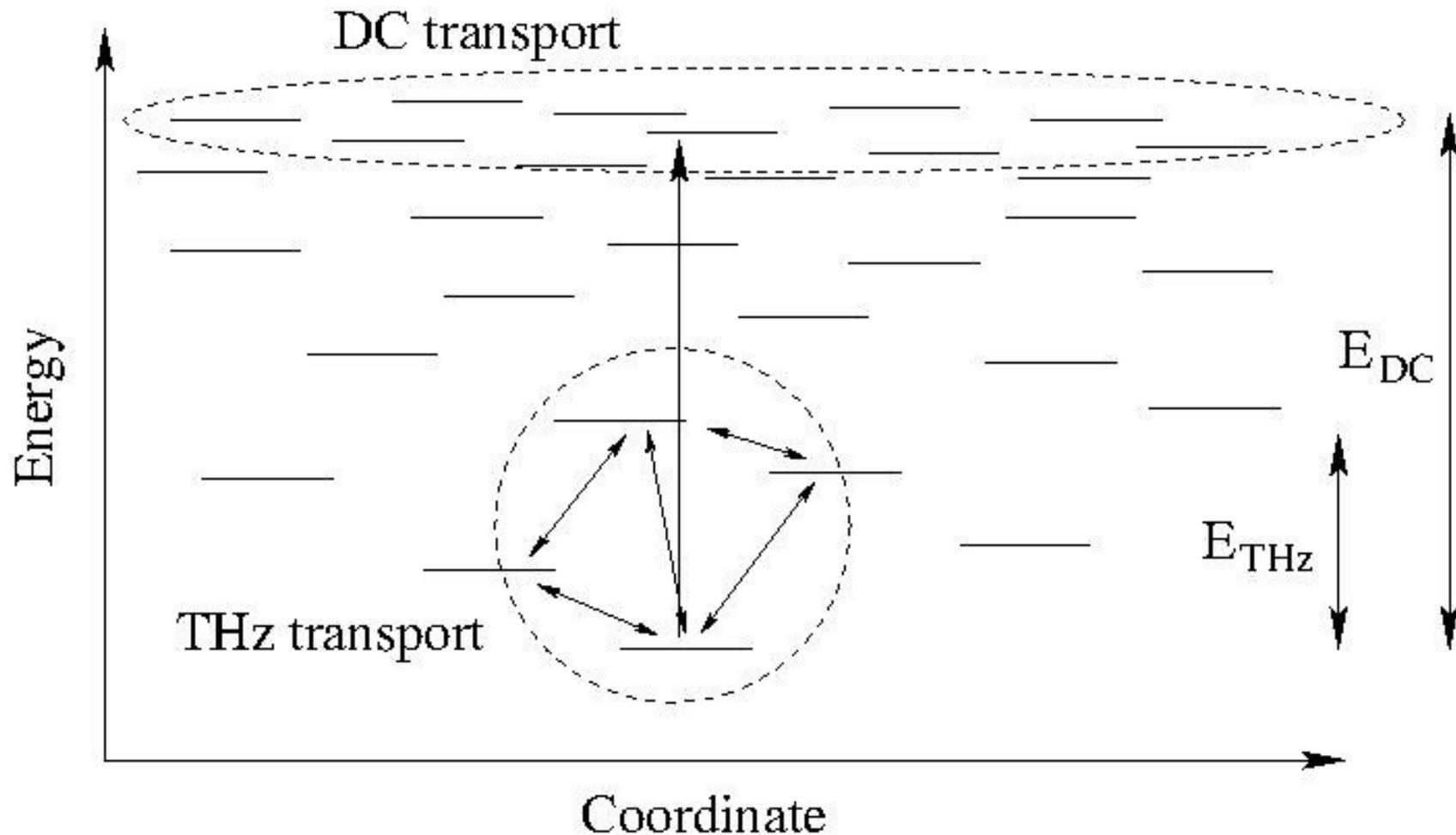


- Temperature dependence



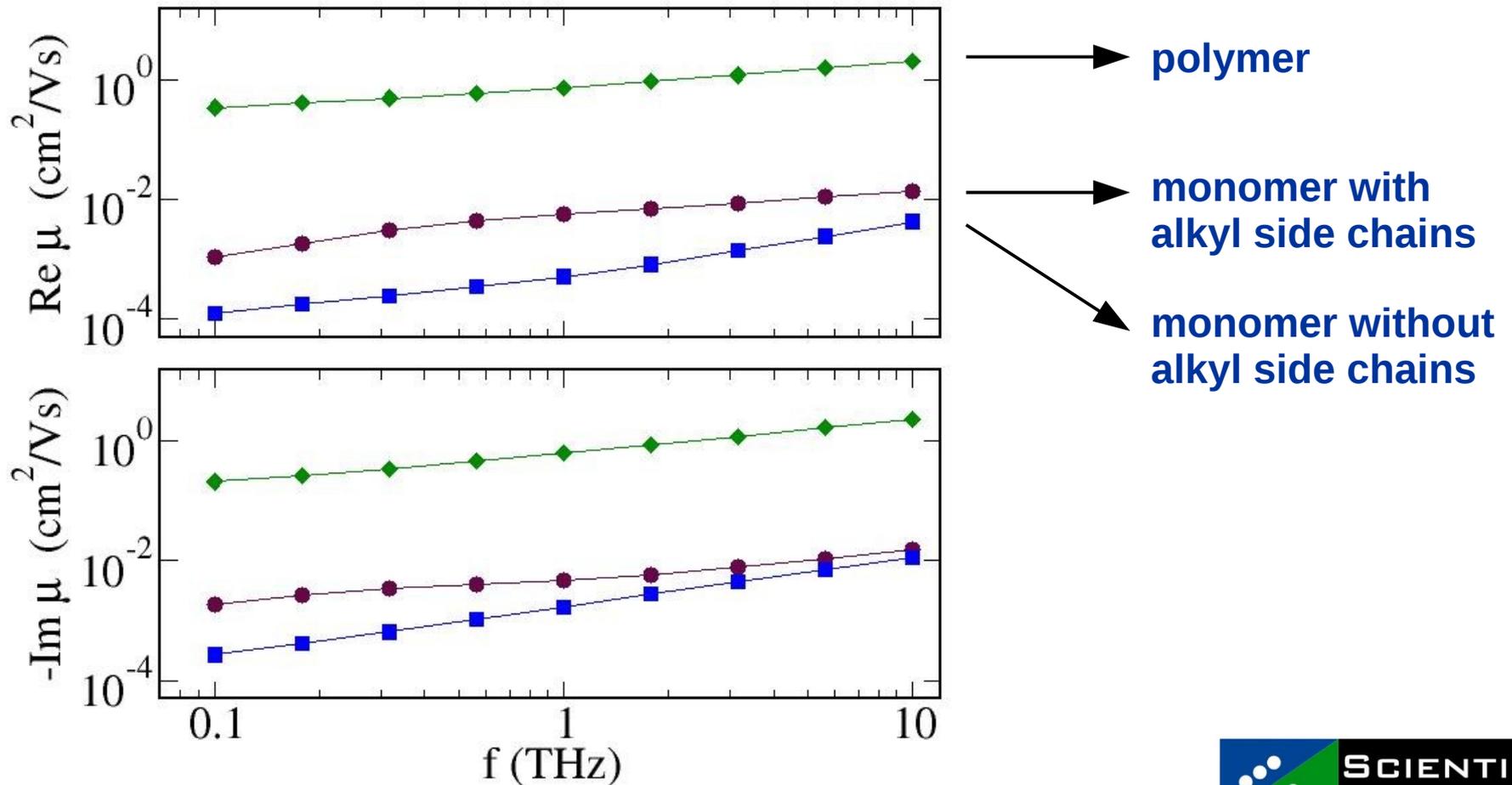
- Thermally activated transport, but with a much smaller activation energy (~115meV) compared to the DC case (~250meV).

Schematic comparison of DC and THz transport

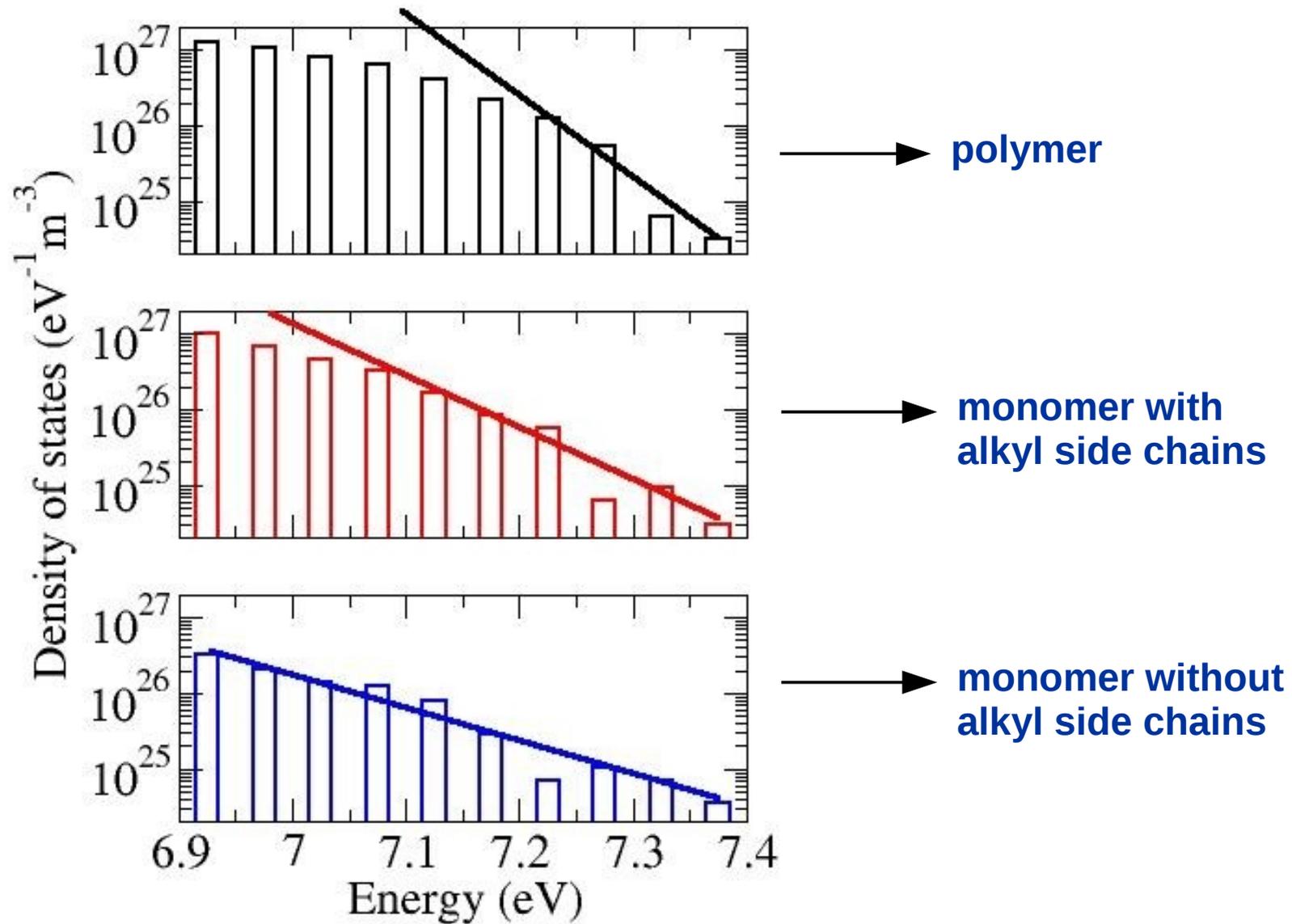


Comparison of THz mobilities of similar materials

- APFO-3 polymer material with alkyl side chains
- APFO-3 monomer material without alkyl side chains
- APFO-3 monomer material with alkyl side chains



Energetic disorder as the origin of this behaviour



Summary

- **Identification of the origin of THz mobility**
 - **How far are carriers probed by THz radiation traveling?**
 - **Answer: high f – 1 or 2 hops, low f – transport over $\sim 10\text{nm}$**
 - **What are they hopping times?**
 - **Answer: above THz hopping rates are present**
- **Identification of parameters that affect the THz mobility**
 - **Energetic disorder**
 - **Answer: Reduces THz mobility**
 - **Temperature**
 - **Answer: Thermally activated transport but with significantly smaller activation energy than for DC transport**
 - **Presence of side chains**
 - **Answer: Reduces disorder and increases THz mobility**

Pros and cons of the whole approach

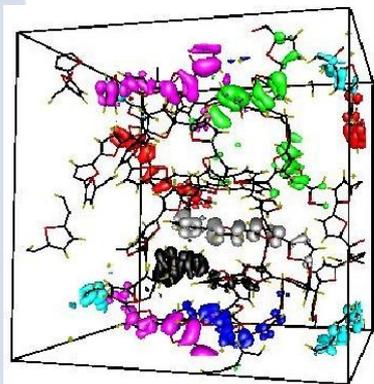
- **Pros:**

- **No free parameters.**
- **Good for comparison of two similar materials.**
- **Microscopic view of the material – provides insight into the microscopic processes.**

- **Cons:**

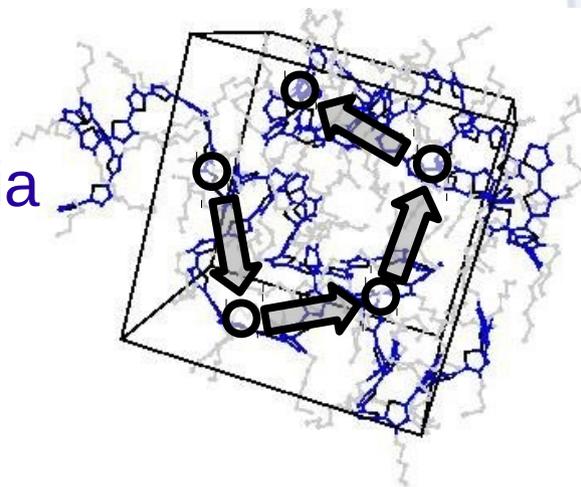
- **Computationally rather demanding.**
- **Uncertainty in the morphology of the material.**

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