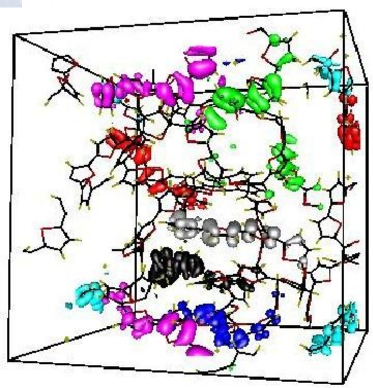
Multiscale simulations of the density of states, DC and THz mobility of charge carriers in disordered conjugated polymers



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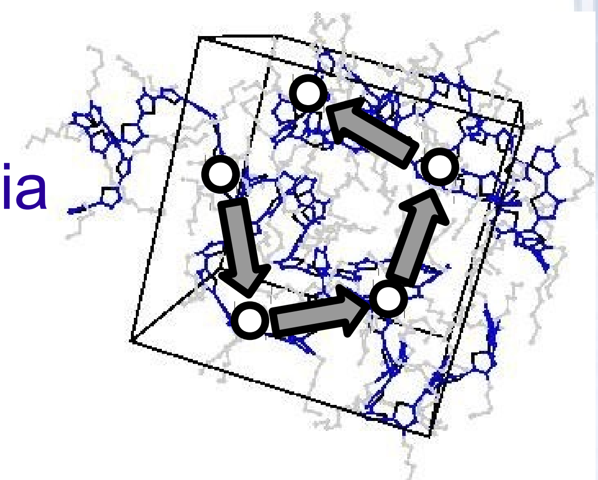

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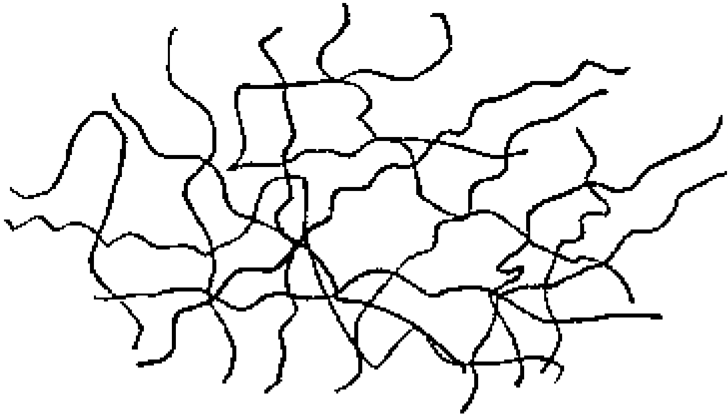
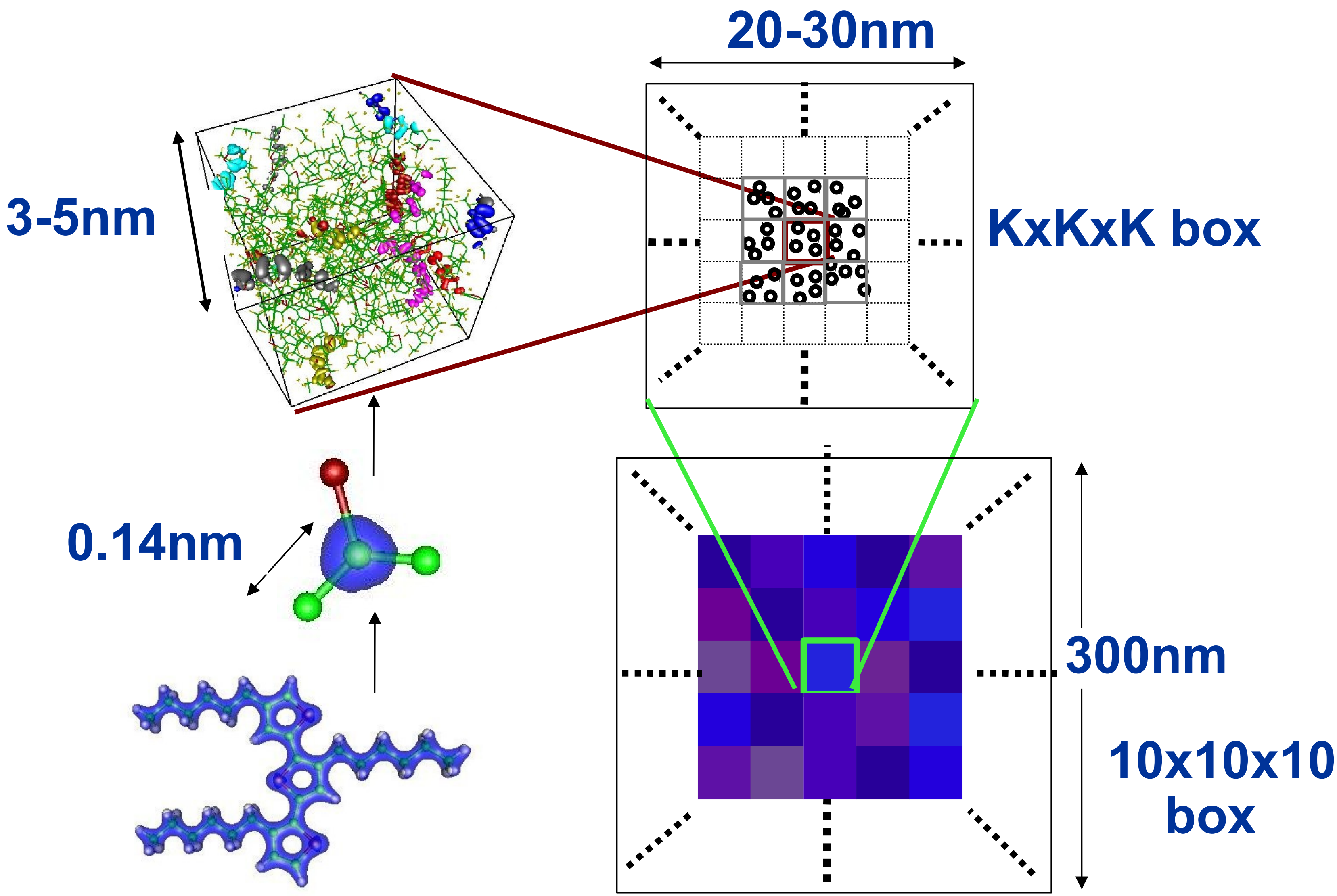
Introduction

- Mobility at high (THz) frequencies is more relevant than DC mobility in many cases (e.g. bulk heterojunctions)
- In this work
  - Extension of previous atomistic multiscale methodology for simulation of DC transport in disordered polymers.
  - Identification of the origin of THz mobility
    - How far are carriers probed by THz radiation traveling?
    - 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.

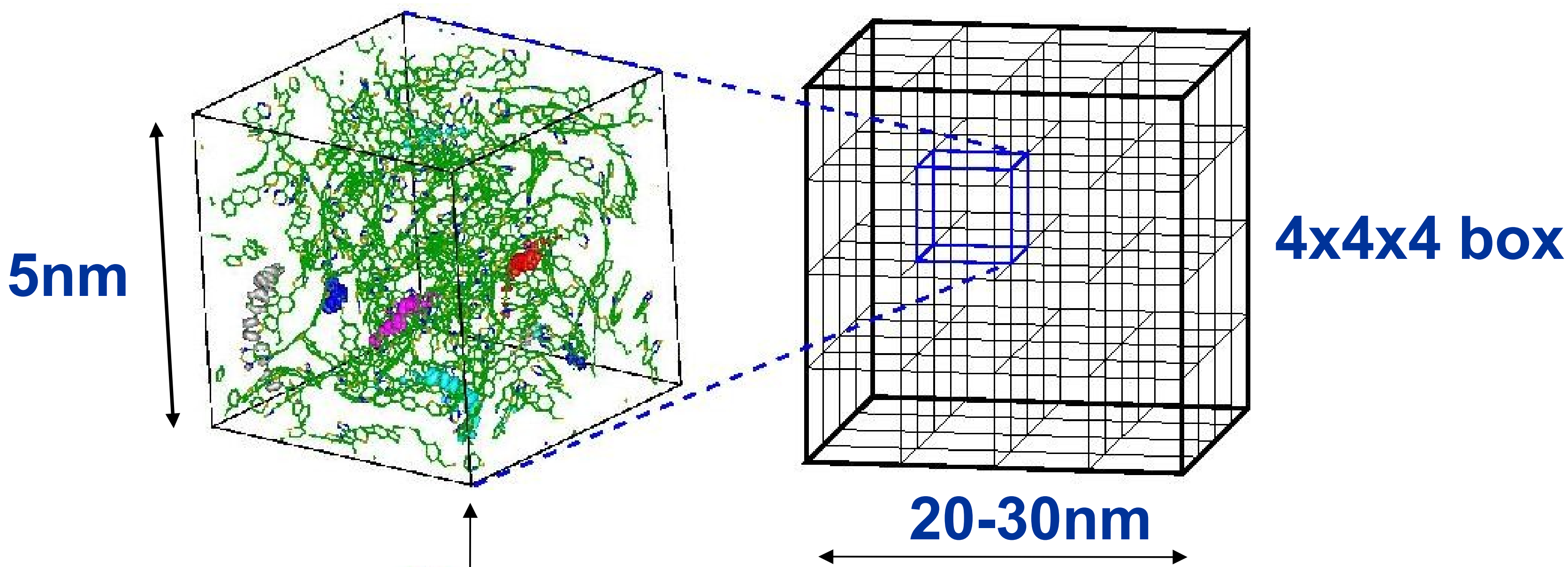


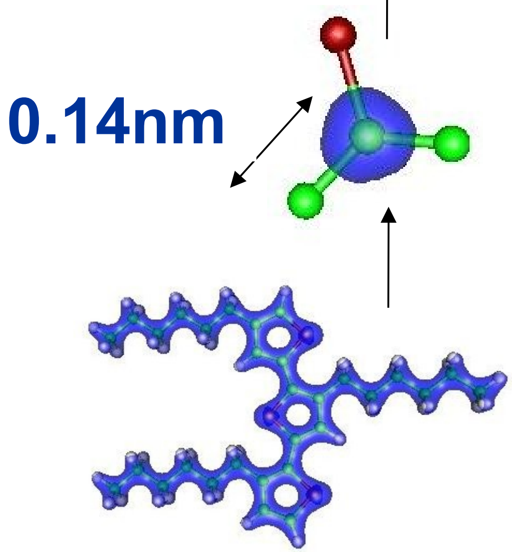
Multiscale method for DC carrier transport



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

Multiscale method for THz carrier transport





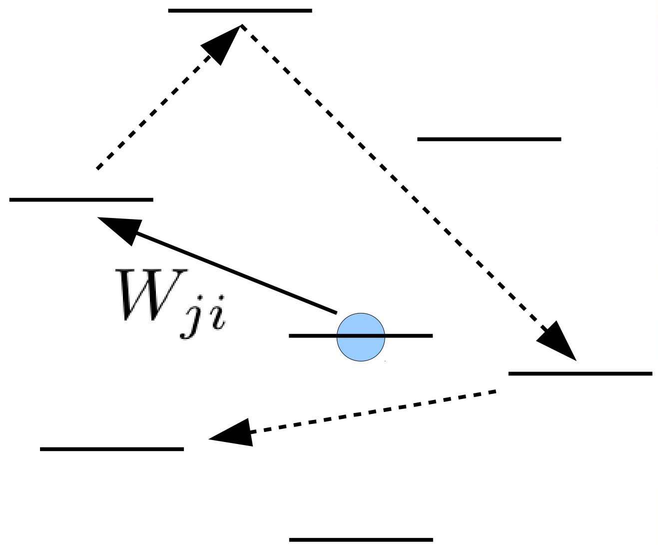
- THz radiation probes the transport over short length scales, therefore 20 nm box is big enough

Calculation of terahertz mobility

- **Rate equations for populations of electronic states**

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_j A_{ij} n_j$$

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



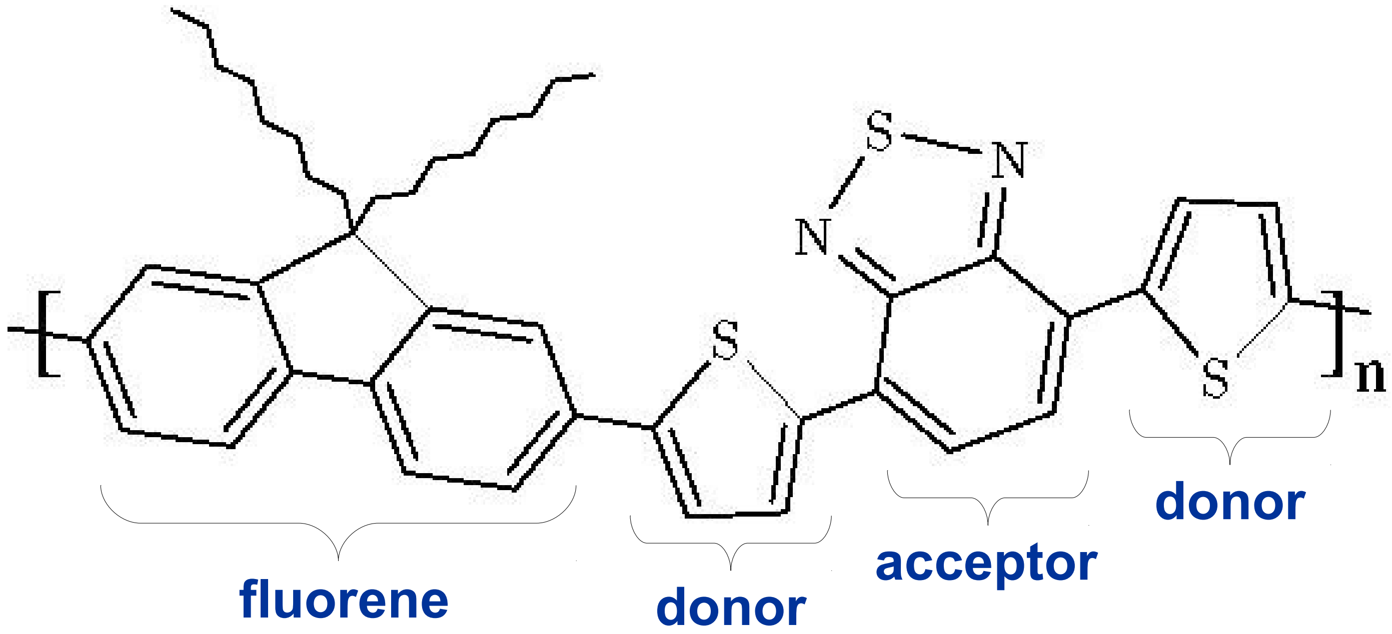
- **Kubo's linear response formula**

$$\mu(\omega) = -\frac{e\omega^2}{2k_\mathrm{B}T} \int_0^\infty \mathrm{d}t e^{i\omega t} \langle \Delta^2(t) \rangle$$

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

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)
- Experimental data on THz mobility available (University of Lund, Villy Sundstrom group).

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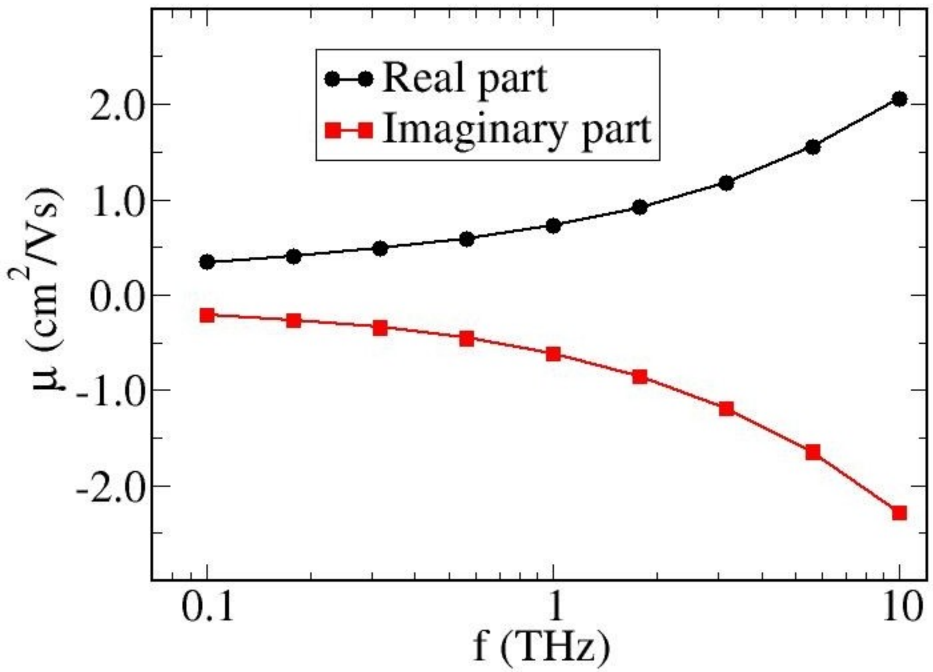
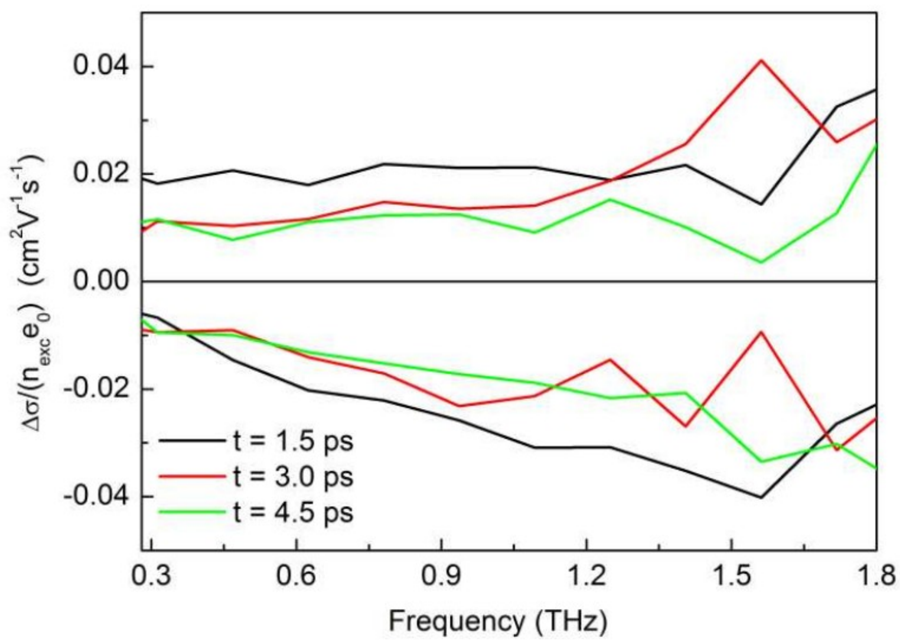
Frequency dependence of mobility at 300K

- Hole mobility in APFO-3



simulation



experiment (University of Lund, Sundstrom group)

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

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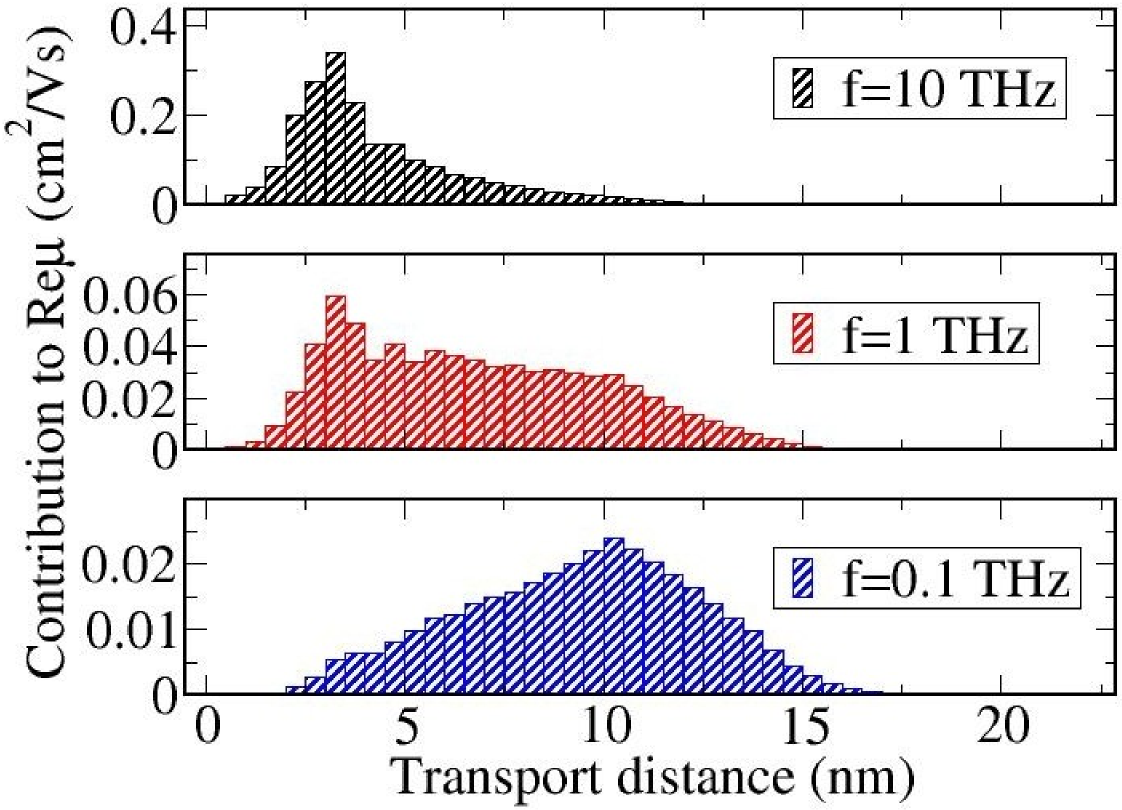
What does THz radiation actually probe?

- **Distance-resolved mobility:**



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

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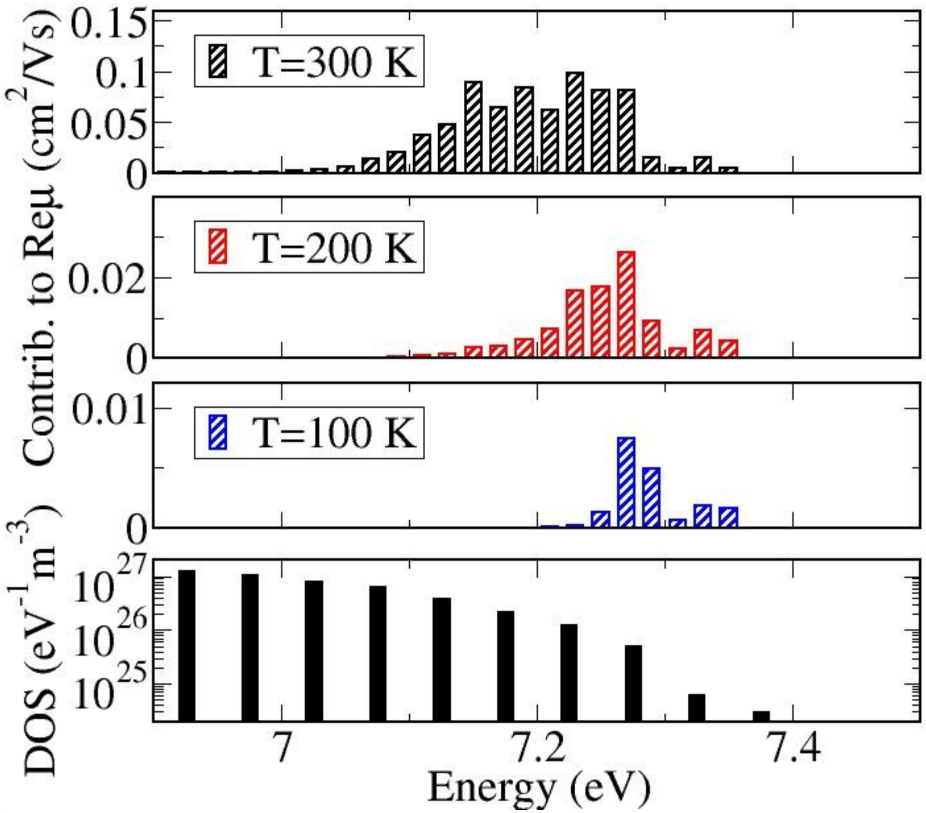
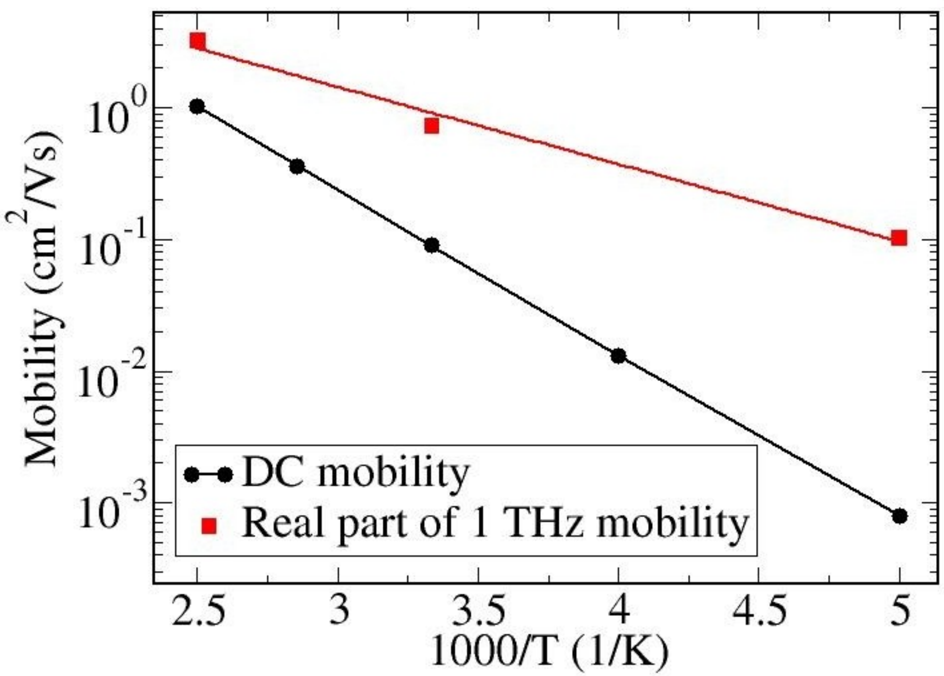
Temperature dependence of THz mobility

- Energy-resolved mobility



- Temperature dependence



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

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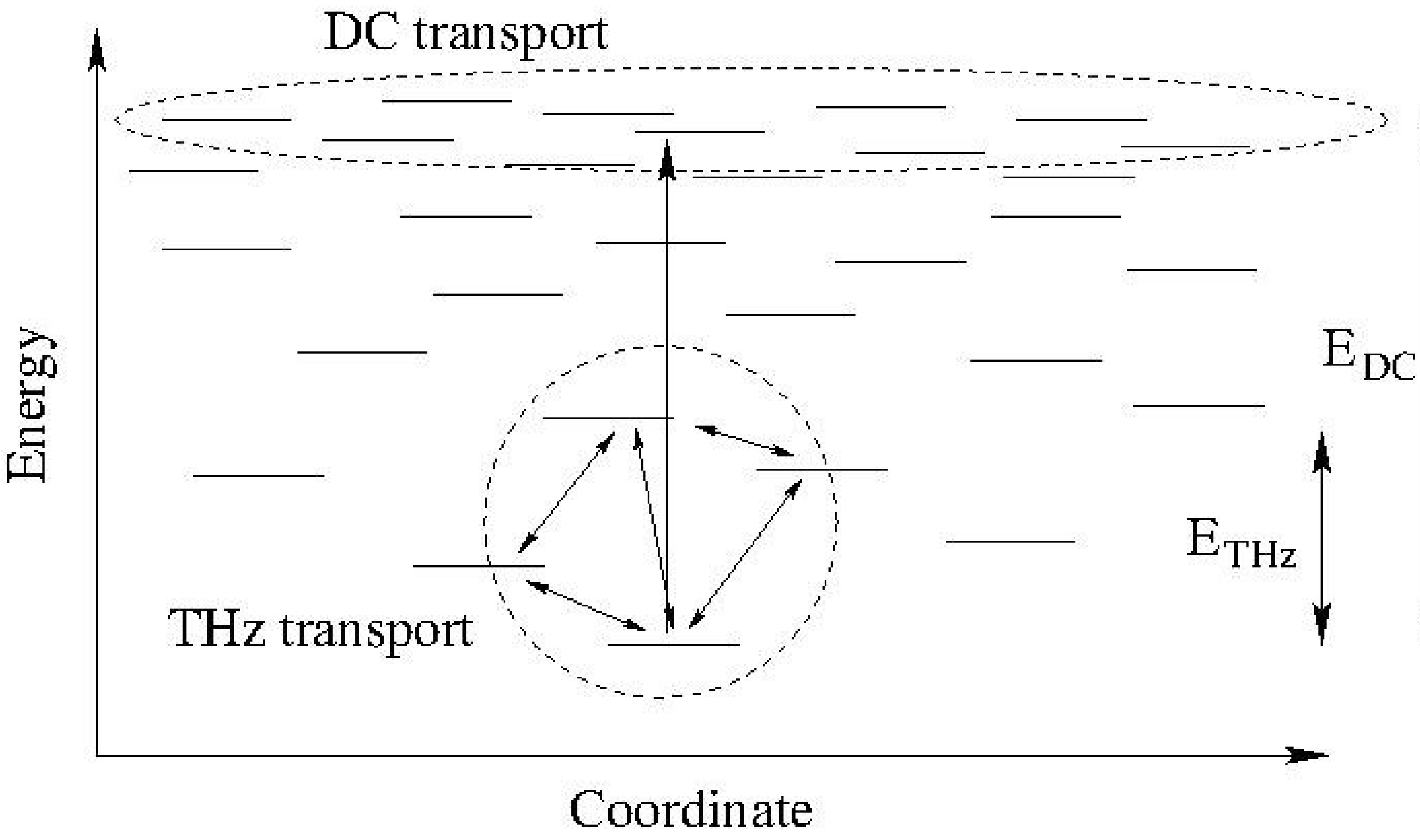
Schematic comparison of DC and THz transport



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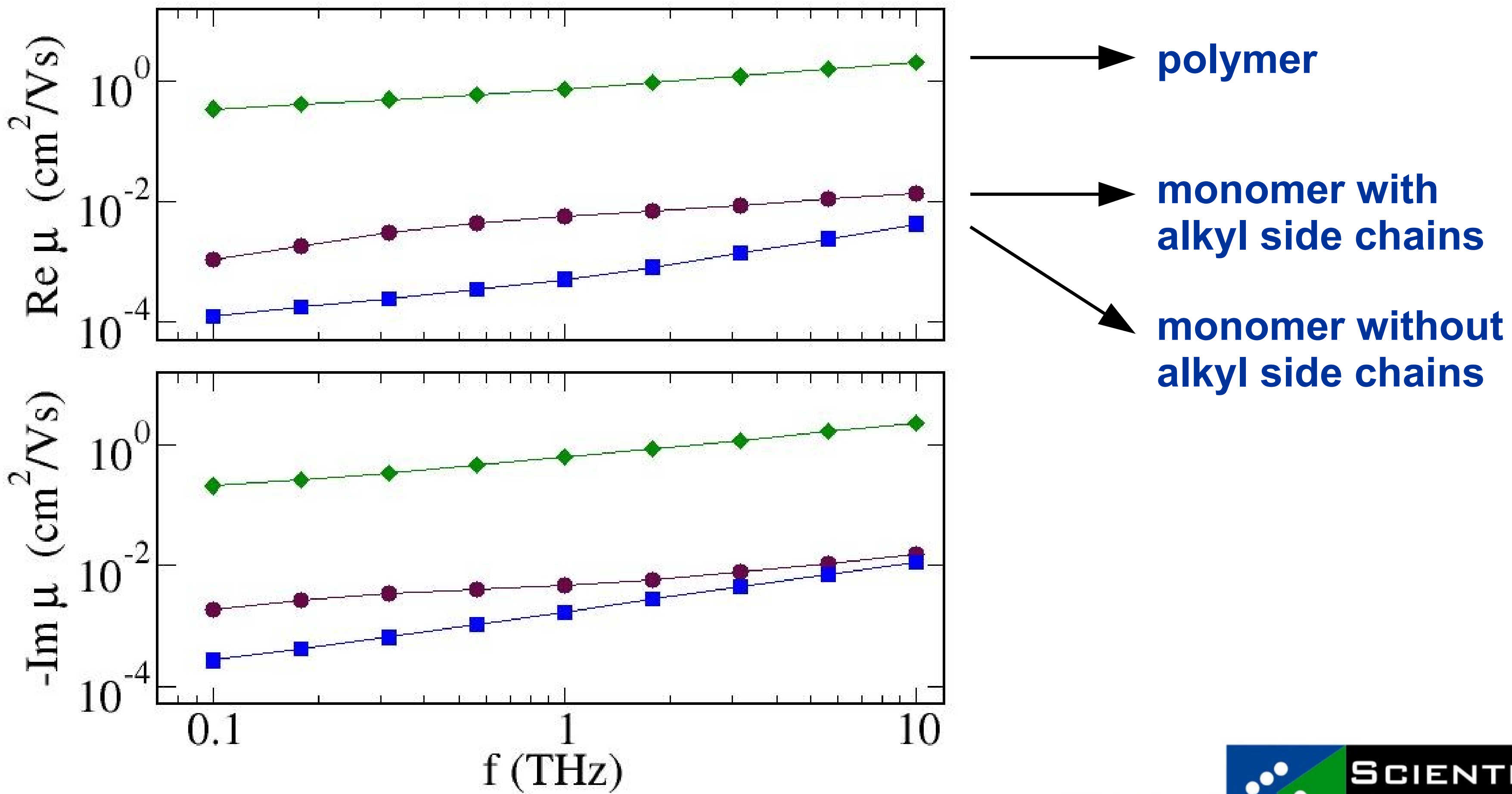
Comparison of THz mobilities of similar materials

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



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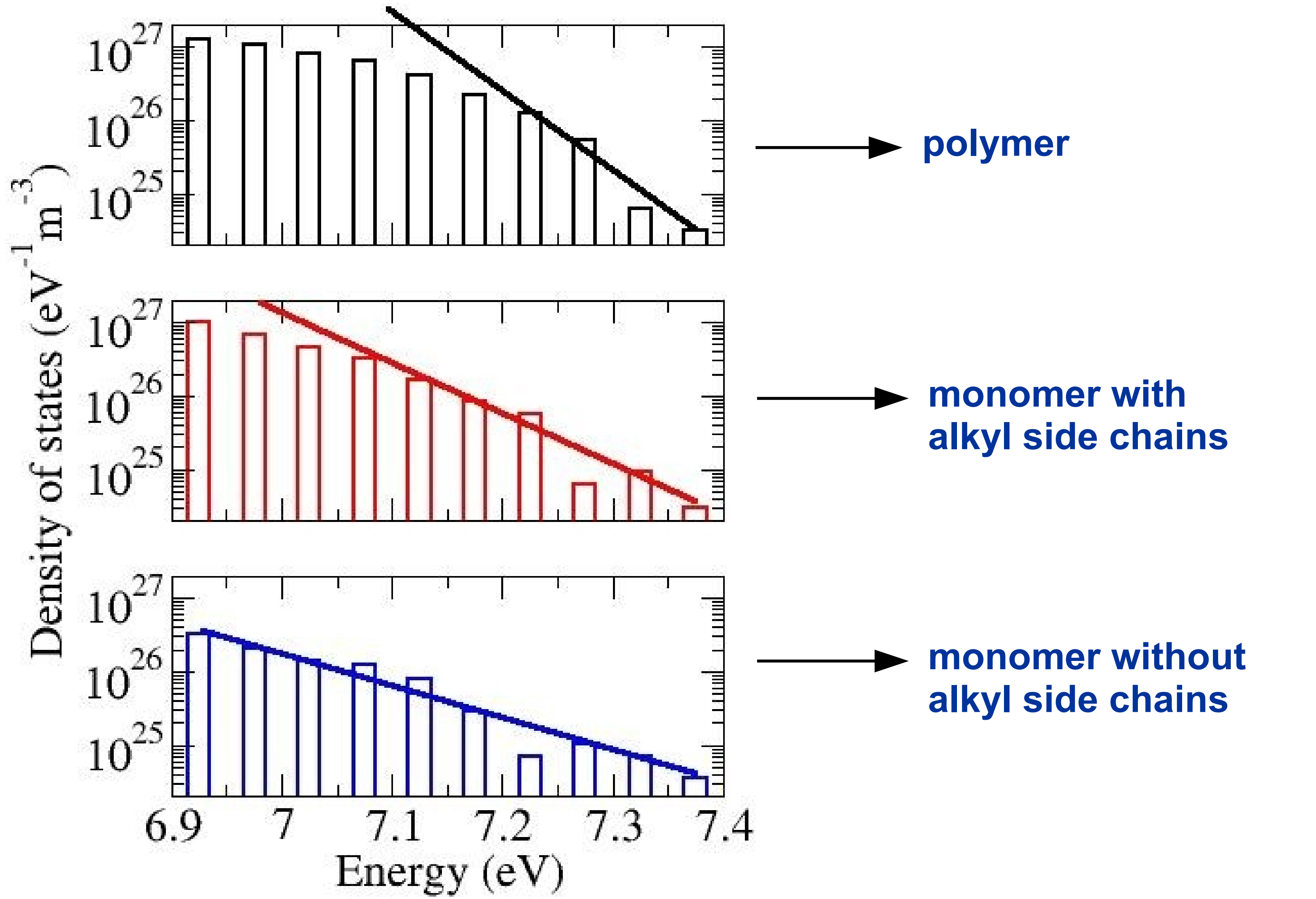
Energetic disorder as the origin of this behavior



Conclusion

- 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 ~10nm
  - 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

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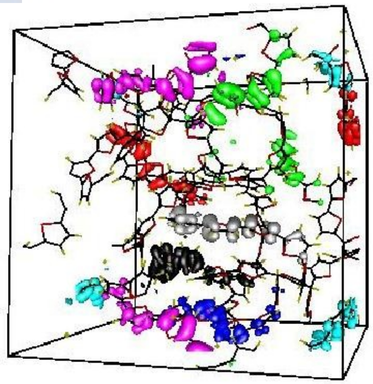

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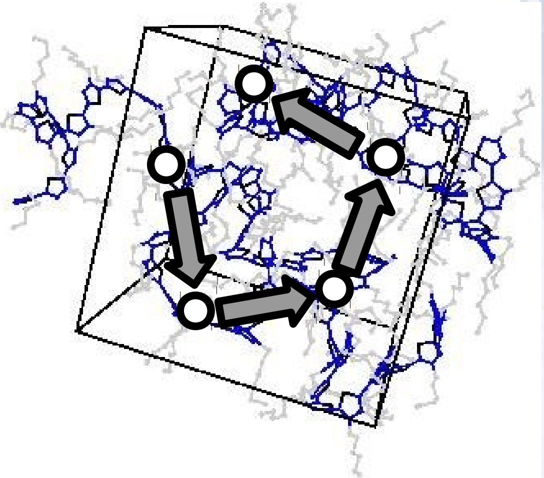

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