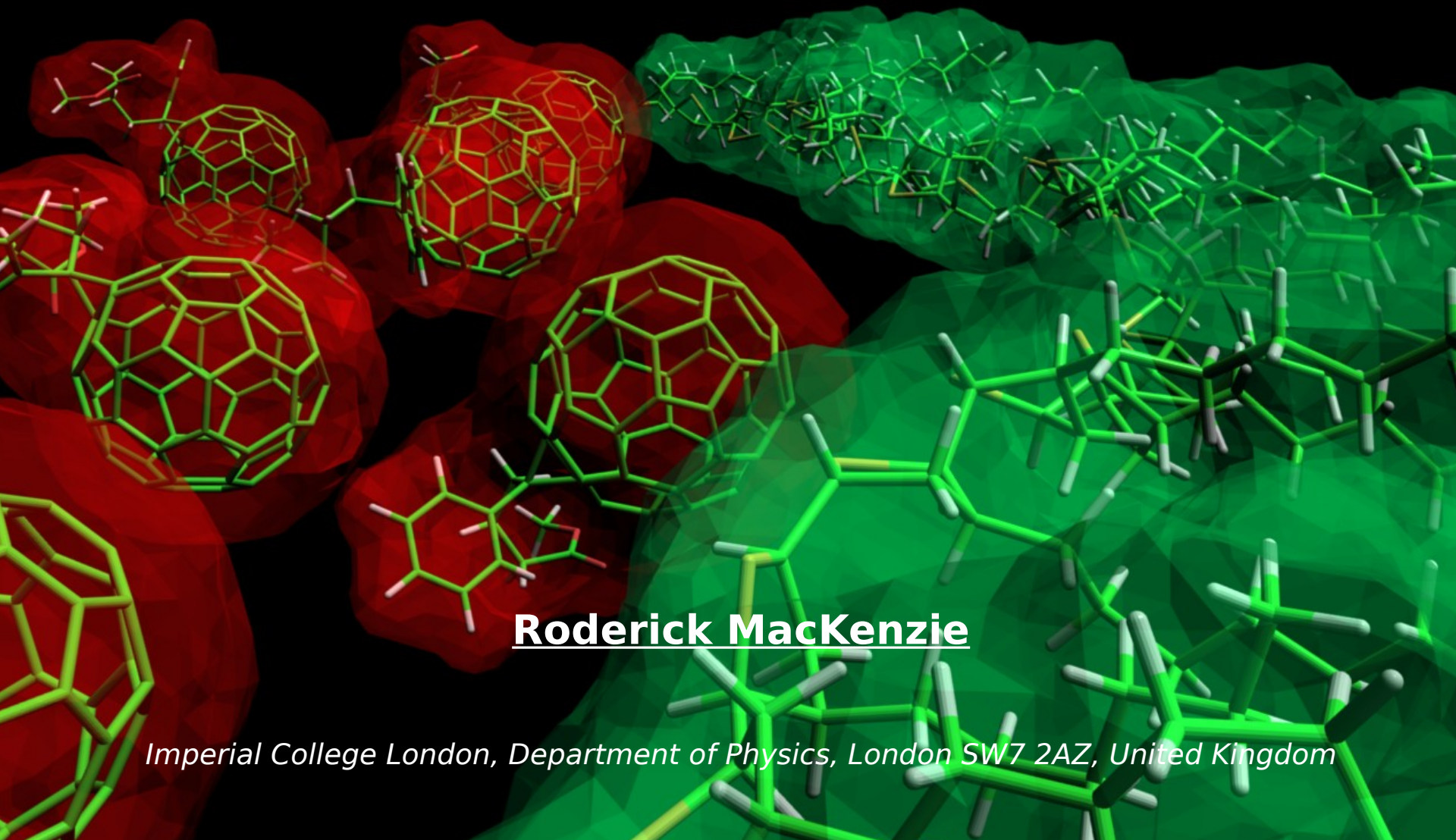
Recombination and transport in OPVs (part II)



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Overview

1) Molecular level simulation of thin films

2) Introduction to device models.

3) Electrical characterization of OPVs
- Charge extraction
- Transient photo-voltage
- Transient photo-current

4) Diffusion limited recombination in OPVs
- Langeving recombination
- Shockley-read-hall recombination

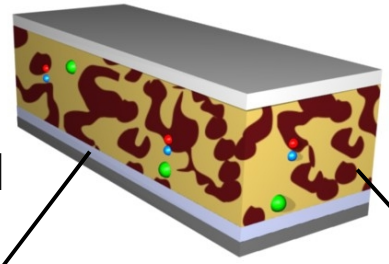
5) A device model

6) The open circuit voltage

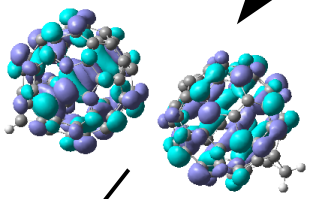
7) Conclusions

www.roderickmackenzie.eu/leacturenotes.html

Modeling organic semiconductors



Molecular level simulation



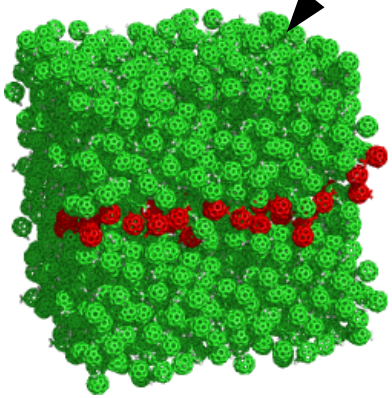
Device level simulation

$$\nabla \epsilon_o \epsilon_r \cdot \nabla \phi = q \cdot (n - p)$$

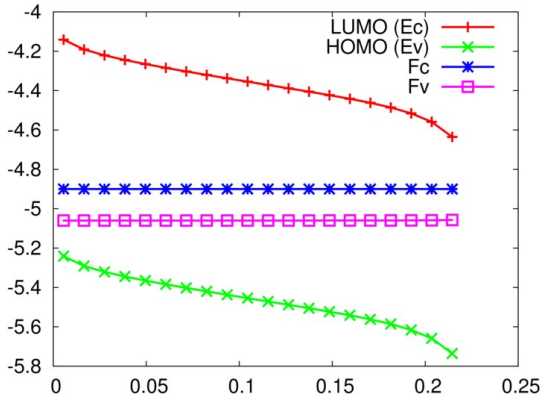
$$J_n = q \mu_e n \nabla E_c + q D_n \nabla n$$

$$J_p = q \mu_h p \nabla E_v - q D_p \nabla p$$

Drift diffusion or Maxwells equations



Molecular dynamics or quantum chemistry



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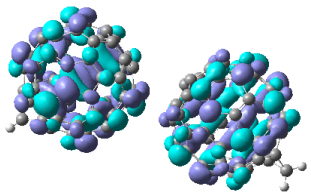
Modeling organic semiconductors



$$\nabla \epsilon_{o\ r} \cdot \nabla \phi = q \cdot (n - p)$$

$$J_n = q\,\mu_e\, n \nabla E_c + q D_n \nabla n$$

$$J_p = q\,\mu_h\, p \nabla E_v - q D_p \nabla p$$

Molecular dynamics and quantum chemistry

Advantages:
We can model and understand individual molecules.

Disadvantages:
It is too computationally slow to look at whole devices. We are limited to small systems of thousands of molecules at most.

Drift diffusion simulations

Advantages:
It is fast enough to look at a whole device and understand why it performs as it does.

Disadvantages:
It sweeps lots of the interesting physics in to single fitting parameters and can not provide molecular level insight.

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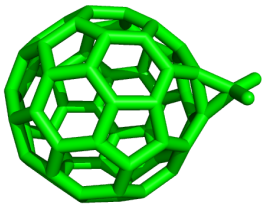
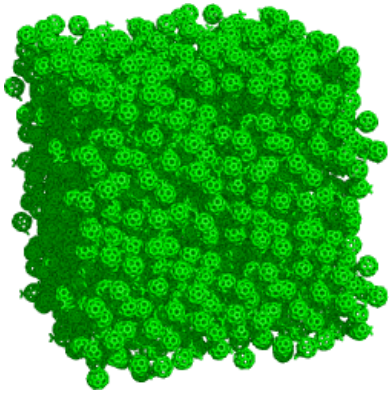
Calculating mobility in thin films from first principles

Molecular structure



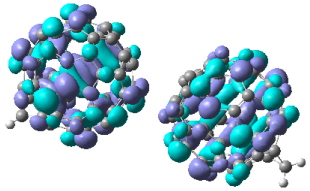
Generating the film (Molecular Dynamics)

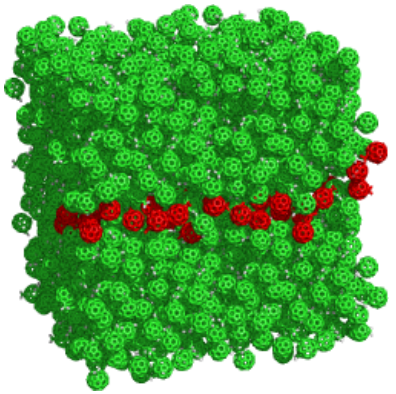
Simulated material structure



Find interacting molecular pairs (~1500)

Calculate Electronic hopping rate between **all** pairs of neighbouring molecules





Perform time of flight (**Monte-Carlo**) simulations

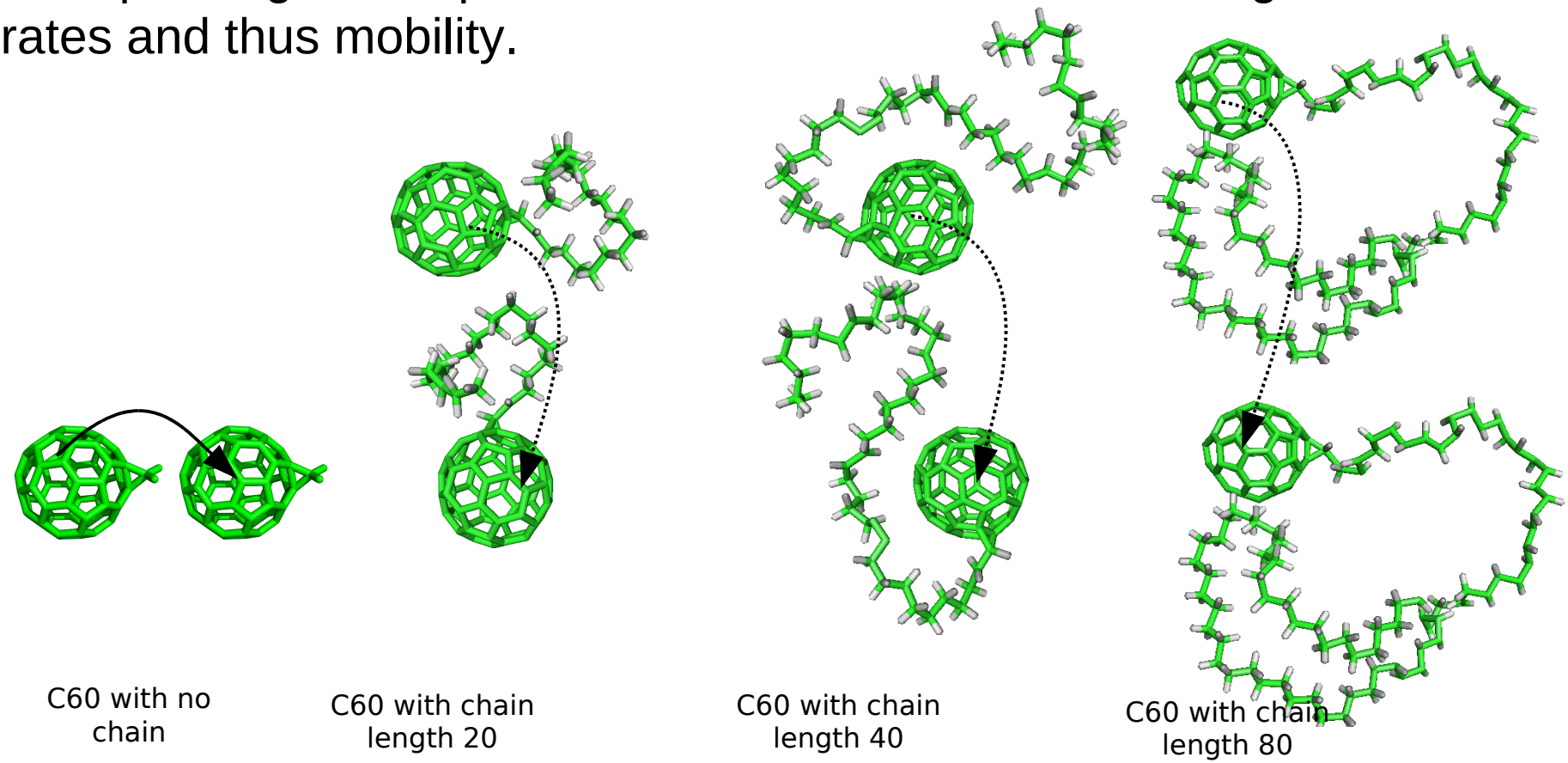
$$\mu(T,F) = \frac{L}{F} \cdot \left\langle \frac{1}{t} \right\rangle$$

Calculated material Mobility

μ: Mobility
L: Sample length
F: Electric field
t: Time of flight

Generating the film (1/3): Why is the morphology important?

- The shape of a molecule determines how it will pack.
- The packing will help determine the intermolecular charge transfer rates and thus mobility.



C60 with no chain

C60 with chain length 20

C60 with chain length 40

C60 with chain length 80

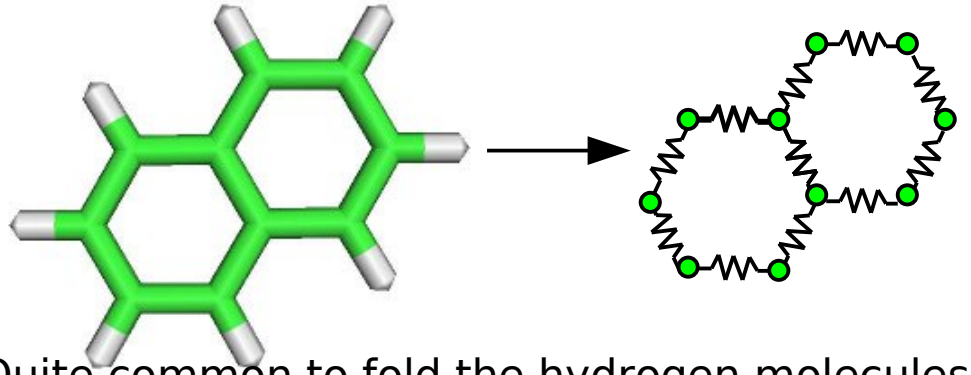
MacKenzie et al. J. Chem Phys 132, 064904, 2010

Generating the film (2/3): Molecular dynamics an overview

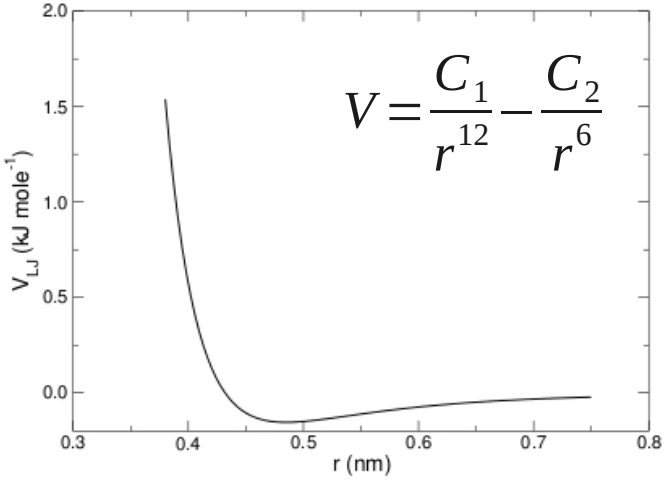
•MD assumes that molecular interactions can be described with Newtonian Mechanics.

$$m_i \frac{\partial^2 \boldsymbol{r_i}}{\partial t^2} = F, i = 1..N$$

•Atoms within molecules are described as masses and springs.
•Van der Waals and Coulomb interactions are introduced by potential fields.
•The force fields are often derived from quantum calculations so they can be quite accurate.



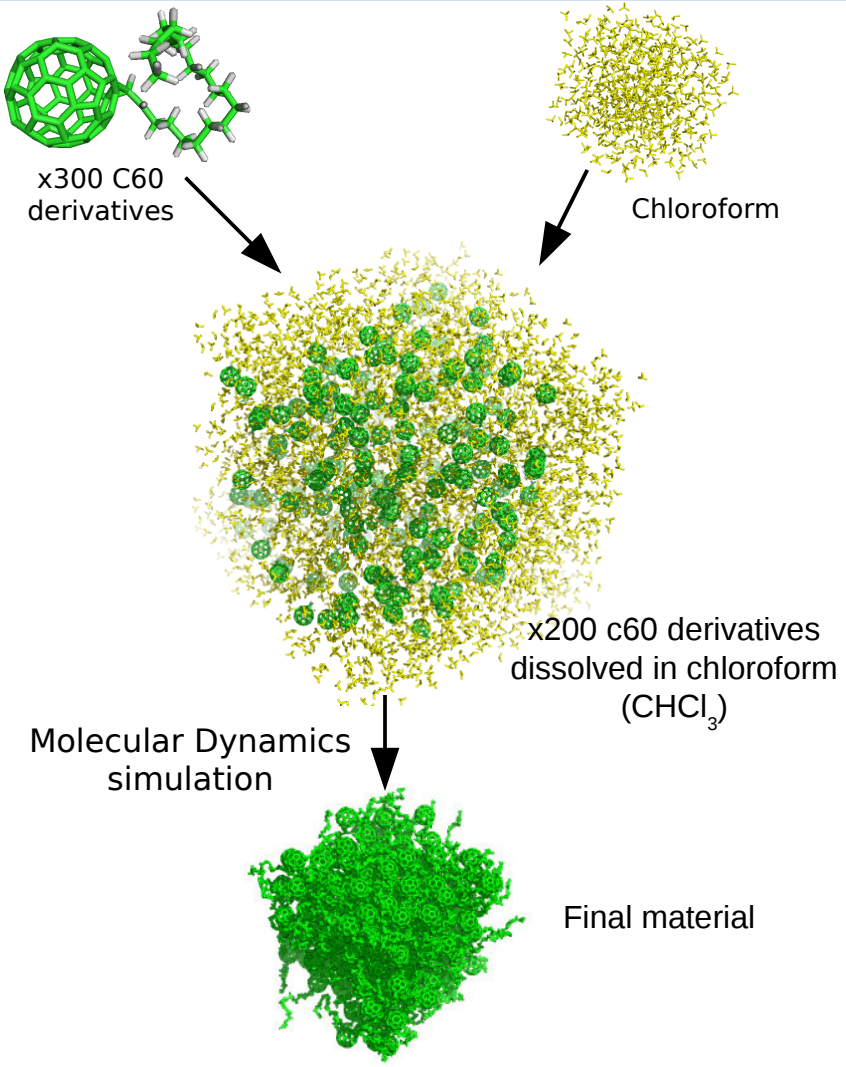
Quite common to fold the hydrogen molecules in to the carbon atoms.



The Lennard-Jones interaction
www.gromacs.org

Generating the film (3/3): Simulating molecular packing.

- To generate a morphology:
  - ~ a few hundred molecules are placed in a solvent.
  - Atmospheric pressure is applied (100 kPa).
  - Solvent is gradually removed.
  - Thus **evaporation is simulated**
- Such a process would occur in spin coating
- If a solvent is not used the molecules stick together in clumps



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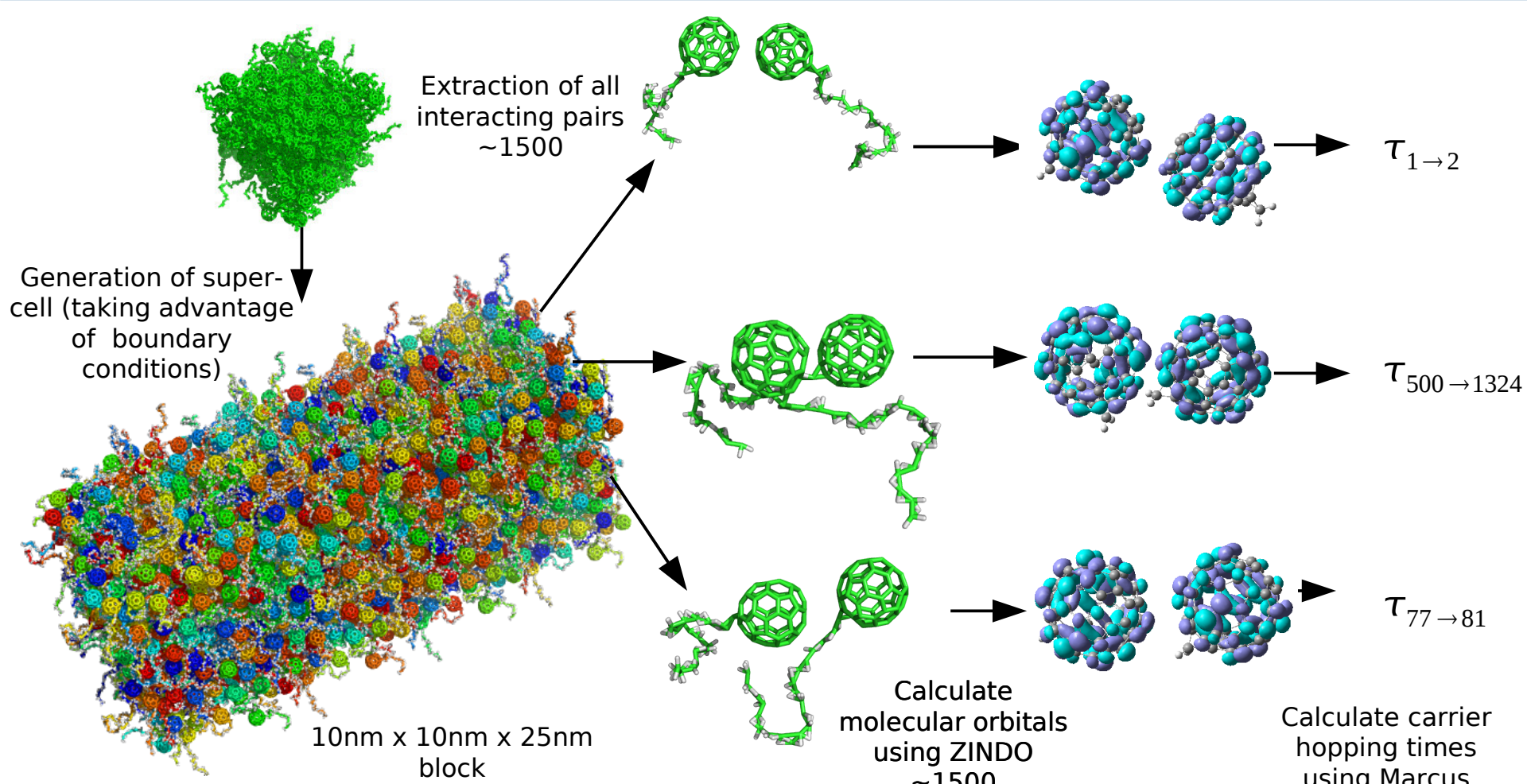
Calculation of carrier hopping times



•Super-cell reduces impact of diffusion current

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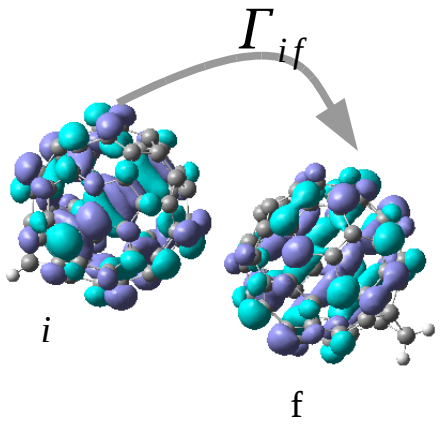
Calculation of the carrier hopping rates using Semi-classical Marcus Theory

- The molecular structure has been calculated
- The intermolecular electron transfer need to be calculated
- For this Semi-classical Marcus Theory is used

$$\Gamma_{if} = 2\pi |J_{if}^2| (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(-\frac{(\Delta E + \lambda)^2}{4\lambda\kappa_B T}\right)$$

Marcus's carrier transfer equation



Chem. Rev. 2004, 104, pp. 4971-5003

Electronic coupling

$$J_{if} = \langle \phi_i | H_e | \phi_f \rangle$$

Driving force ΔE

$$\Delta\epsilon = \langle \phi_f | H_f | \phi_f \rangle - \langle \phi_i | H_i | \phi_i \rangle$$

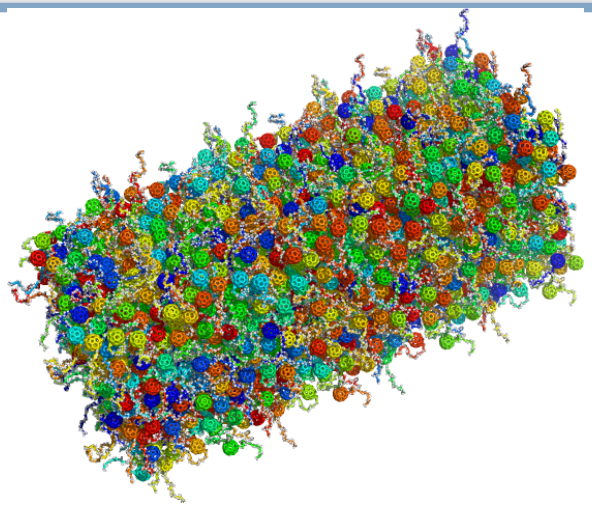
$$\Delta E = \Delta\epsilon + q(\boldsymbol{r} \cdot \boldsymbol{F})$$

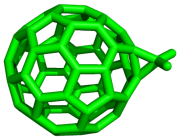
Parameters

λ Reorganization energy
T temperature
κ_B Boltzmann's constant

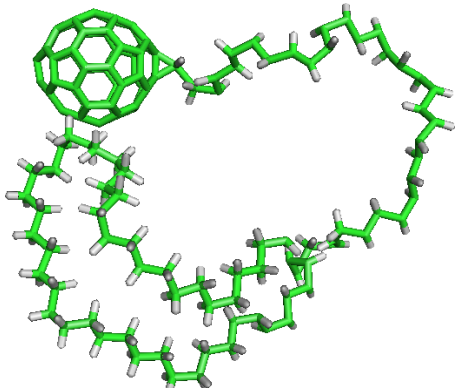
All parameters can be calculate using DFT

Distribution of J

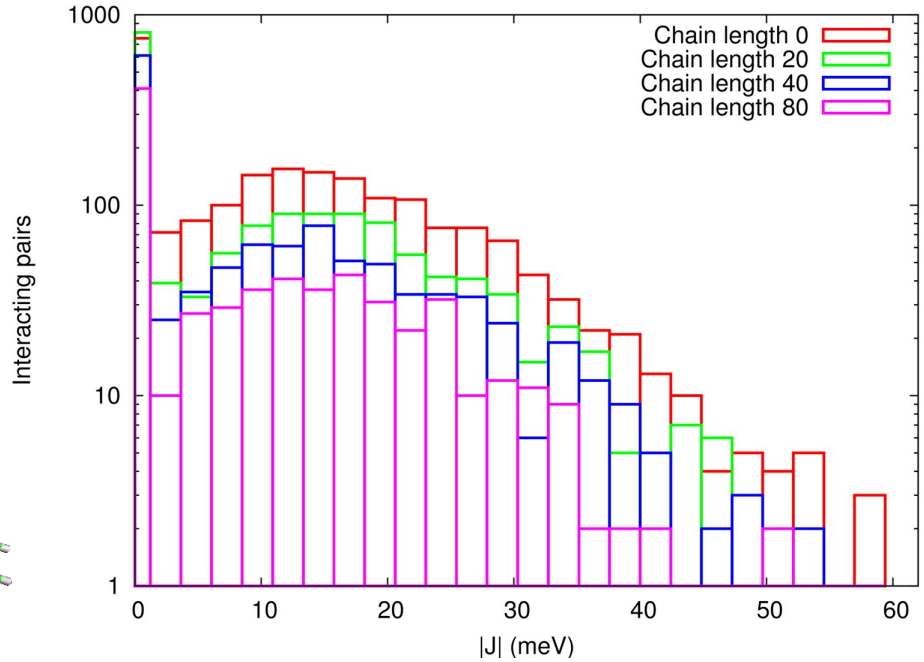




C60 with no chain



C60 with chain length 80



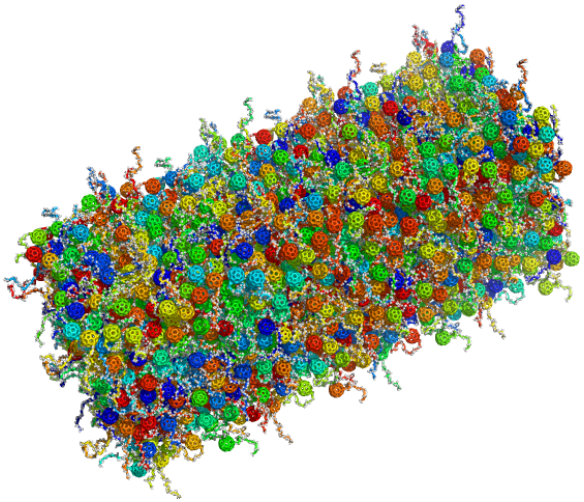
$$J_{if} = \langle \phi_i | H_e | \phi_f \rangle$$

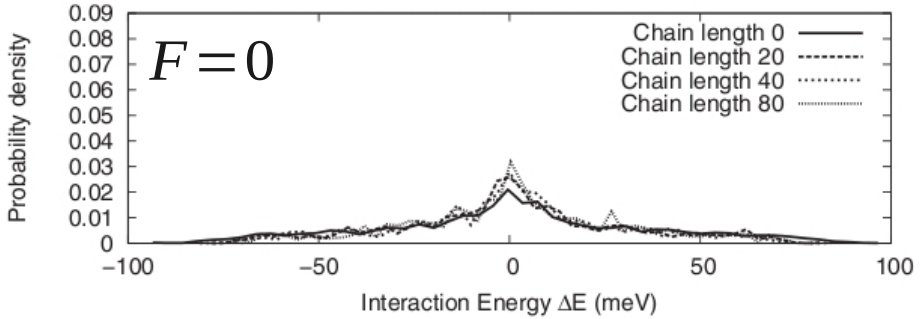
$$\Gamma_{if} = 2\pi |J_{if}^2| (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(-\frac{(\Delta E + \lambda)^2}{4\lambda\kappa_B T}\right)$$

J=Overlap of molecular wave functions

MacKenzie et al. J. Chem Phys 132, 064904, 2010

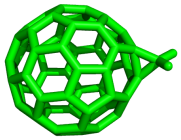
Distribution ΔE



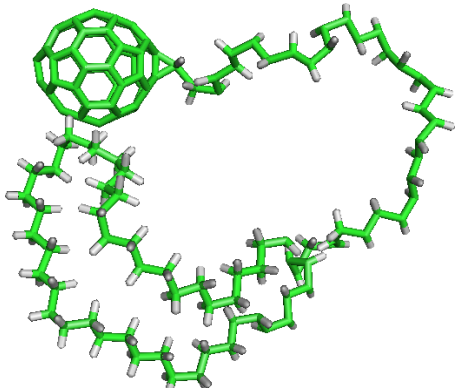


$$\Delta E = \langle \phi_f | H_e | \quad _f \rangle - \langle \quad _i | H_e | \quad _i \rangle + q(\boldsymbol{r} \cdot \boldsymbol{F})$$

$$\Gamma_{if} = 2\pi |J_{if}^2| (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(-\frac{(\Delta E + \lambda)^2}{4\lambda\kappa_B T}\right)$$



C60 with no chain

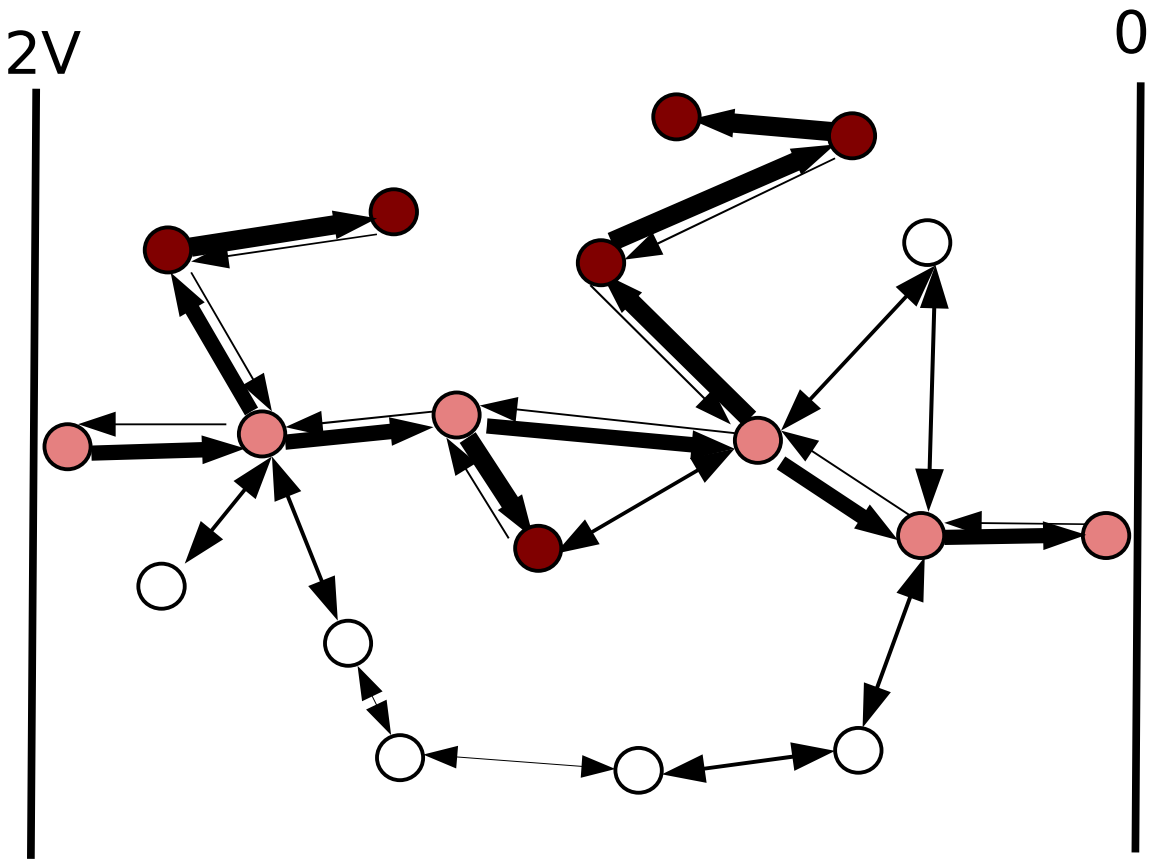


C60 with chain length 80

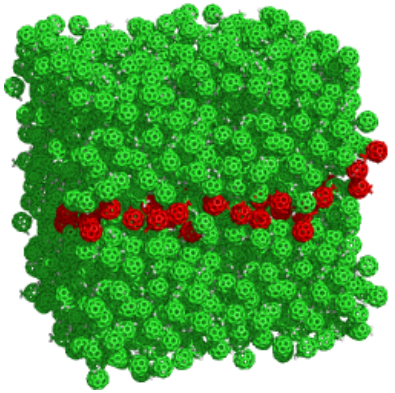
ΔE=Hopping site energy differences

MacKenzie et al. J. Chem Phys 132, 064904, 2010

Charge transport and trapping



- Arrow thickness represents probability of hop.
- Some sites will act as energetic traps or dead ends.
- We believe that around 90% of the charge in an OPV is stuck in these traps.



$$\mu(T,F) = \frac{L}{F} \cdot \left\langle \frac{1}{t} \right\rangle$$